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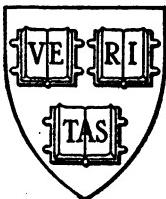
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[CONTRIBUTION FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

ON SOME ADDITION-REACTIONS OF THIO ACIDS.

BY HENRY L. WHEELER.

Received June 3, 1901.

The appearance of an article by A. Eibner¹ on a halogen-substituted aminomercaptan, in which some addition-reactions of thioacetic acid to compounds containing the unsaturated grouping C=N are described, has induced the writer to publish an account of some experiments which have been done here along similar lines. In the article referred to, it is shown that thioacetic acid acts on trichlorethylidendiphenamine,



with the formation of acetanilide, hydrogen sulphide and a compound which is said to have the properties of acetylphenyl- α -aminotrichloethyl mercaptan. It is also stated that benzylidene-aniline unites with thioacetic acid to form the addition-product, $\text{C}_6\text{H}_5\text{CH}(\text{SH})\text{NC}_6\text{H}_5\text{COCH}_3$.

It was shown by Wheeler and Barnes² that the phenylhydrazone of diethylthiocarbonic ester, $\text{C}_6\text{H}_5\text{NH}-\text{N}=\text{C}(\text{SC}_2\text{H}_5)\text{OC}_2\text{H}_5$, reacts with thiobenzoic acid, yielding ethylthiolbenzoate, $\text{C}_6\text{H}_5\text{CO}\cdot\text{SC}_2\text{H}_5$, and phenylthiolcarbazinic ethyl ester,

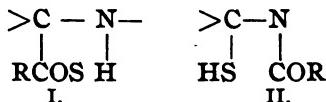


This reaction evidently involves a sort of addition different from

¹ *Ber. d. chem. Ges.*, 34, 656 (1901).

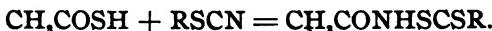
² *Am. Chem. J.*, 24, 62 (1900).

that described by Eibner. These two modes of addition can be represented as follows :



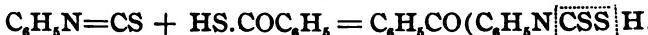
The ease with which Eibner's addition-products give acetanilide indicates that the addition takes place according to (II). The possibility, however, that they may have the structure $\text{RCH}(\text{SCOCH}_3)\text{NHC}_6\text{H}_5$, and that the addition takes place according to (I) is not excluded by the evidence thus far produced.

Chanlaroff¹ found that thioacetic acid combines with the $-\text{C}\equiv\text{N}$ group in thiocyanates; and in papers from this laboratory it has been proved that the addition takes place according to (II),



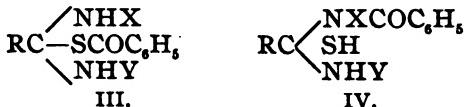
It has been shown by Wheeler and Merriam² that isothiocyanates, $\text{RN}=\text{CS}$, in general, react readily and quantitatively with thioacetic and thiobenzoic acid, even in boiling benzene, yielding substituted amides and carbon disulphide.

The final result of the action in this case is in all probability preceded by the formation of an unstable addition-product, according to (II), which decomposes as follows :



This is confirmed by the fact that thiobenzoic acid and phenyl isocyanate give the addition-product, $\text{C}_6\text{H}_5\text{CO}(\text{C}_6\text{H}_5)\text{NCOSH}$, which can easily be isolated. It may be crystallized from alcohol, and is stable at temperatures below 97°.

Thiobenzoic acid unites with amidines, and, as might be expected, quite stable addition-products or salts result. Whether the addition takes place according to the first method, giving esters of thiobenzoic acid (III), or according to the second, with the formation of diamidomercaptan derivatives (IV), can not be definitely decided at present.



¹ *Ber. d. chem. Ges.*, 15, 1987 (1882).

² This Journal, 23, 283.

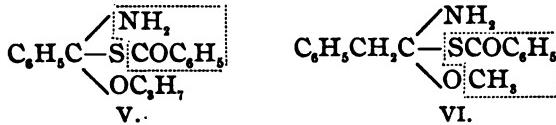
The evidence thus far obtained appears to favor the view that the addition takes place as represented by (III). Such a compound would not separate hydrogen sulphide without decomposition, while if the products have the structure (IV), or are simple pentavalent nitrogen derivatives, they might easily be desulphurized.

The addition-product in the case of diphenylformamidine decomposes on fusion, with evolution of little more than traces of hydrogen sulphide, into thioformanilide and benzanimide. Alkalies remove thiobenzoic acid and not hydrogen sulphide.

The above view receives further support from the behavior of imidoesters. Thiobenzoic acid readily reacts with imidoesters, and the products are a thiol ester and an amide. The reaction evidently takes place by addition to the double union according to I, as in the case of the above-mentioned phenylhydrazone. It may be represented as follows :



That the decomposition proceeds in the above manner, and not as represented by (V), is shown by the behavior of phenylacet-imidomethyl ester towards thiobenzoic acid (VI) :



The amide obtained in the latter case is phenyl acetamide, instead of benzamide, and consequently the esters formed in these reactions are thiol and not thion derivatives.

An analogous reaction takes place in the case of acylpseudo-thioureas. Benzoylpseudobenzylphenylthiourea gave benzoyl-phenylthiourea, when heated on the water-bath with thiobenzoic acid :



Thiobenzoic acid readily reacts with acetonephenyl hydrazone on the steam-bath in an entirely different manner from that of benzoyl chloride¹, and the mixture shows very little loss in weight. *s*-Monobenzoylphenylhydrazine separates in quantity, while only a small amount of dibenzoylphenylhydrazine is

¹ Freer : *Am. Chem. J.*, 21, 18 (1899).

obtained. In addition to this, considerable neutral oil results which cannot be purified by distillation under diminished pressure. The thio acid acts in this case, therefore, according to (II).

The action of thiobenzoic acid on ureas has been examined in the case of diphenylthiourea. It has been shown by Deninger¹ that, in the presence of pyridine, benzoyl chloride and this urea give a dibenzoyl derivative, while, according to Dains,² to produce a reaction without pyridine it is necessary to heat the materials to a high temperature. At 150° phenyl mustard oil and benzanilide are quantitatively obtained.

I have found that thiobenzoic acid acts on this urea in boiling benzene, and that the action is similar to that of benzoyl chloride, although the products obtained are benzanilide, carbon disulphide, hydrogen sulphide, and regenerated diphenylthiourea.

The action can be explained by the assumption that the thiourea contains a C=N group, and that either addition takes place according to II, or, that the acid decomposes the urea into aniline and phenyl mustard oil as the first stage of the reaction.

It has been found, in regard to the use of thiobenzoic acid as a means of introducing the benzoyl group into aryl amines, that it reacts as easily as thioacetic acid³. For example, when mixed with aniline, hydrogen sulphide is evolved in the cold, and benzanilide is quantitatively formed.

On the other hand it combines with ammonia and aliphil amines to form more or less stable salts. The product of the union of thiobenzoic acid and diisobutyl amine, $C_6H_5CO\cdot SH\cdot HN(C_6H_9)_2$, can be repeatedly crystallized from alcohol without evolution of hydrogen sulphide. A similar behavior of the phenylsulphocarbazinic acid salts of aryl and aliphil amines, $C_6H_5NH—NHCS.SH.H_2NR$, has been observed by Busch and Rider.⁴ The former give thiosemicarbazides while the aliphil salts do not. Thiobenzoic acid also reacts on the steam-bath with alcohols and phenols, forming benzoic esters.

EXPERIMENTAL PART.

Benzoylthiolcarbanilic Acid, $C_6H_5CO(C_6H_5)NCO\cdot SH$.—When a

¹ *Ber. d. chem. Ges.*, **28**, 1322 (1895).

² This Journal, **22**, 192 (1900).

³ Pawlewsky : *Ber. d. chem. Ges.*, **31**, 661 (1898).

⁴ *Ber. d. chem. Ges.*, **30**, 843 (1897).

benzene solution of phenyl isocyanate (3 grams) and thiobenzoic acid (3.5 grams) were mixed, heat was evolved and the yellow color of the thio acid disappeared. On cooling, a mass of fine colorless needles separated. These, crystallized from alcohol, melted at 97° - 99° with effervescence and a nitrogen determination gave :

	Calculated for $C_{14}H_{11}O_2NS$.	Found.
Nitrogen.....	5.44	5.35

When this compound was heated, it gave off a combustible gas (COS) and on crystallizing the residue from alcohol, benzanimide melting at 161° was obtained.

Alcoholic ammonia converts this addition-product into ammonium thiobenzoate and phenylurea.

When thioacetic acid was added to para-tolyl isocyanate under similar conditions para-acet toluidine was directly obtained.

Diphenylformamidine and Thiobenzoic Acid (by Bayard Barnes).—When 3 grams of the amidine were dissolved in benzene and 2.1 grams of thiobenzoic acid were added, a mass of colorless needles separated, weighing 4 grams. These melted at 130° - 131° and could be crystallized from benzene or a mixture of benzene and ligroin, with only slight decomposition. A nitrogen determination gave :

	Calculated for $C_{20}H_{15}ON_2S$.	Found.
Nitrogen.....	8.38	8.56

Two grams of this addition-product were melted in an oil-bath at 145° - 150° . On cooling and treating the mass with dilute sodium hydroxide a residue remained which crystallized from alcohol in plates melting at 160° - 161° (benzanimide). On adding hydrochloric acid to the alkaline extract a precipitate was obtained which crystallized from alcohol in plates and melted at 137° - 138° (thioformanilide). When the addition-product was treated with alkali, diphenylformamidine was obtained.

Benzylmonophenylamidine and Thiobenzoic Acid (by Bayard Barnes).—This product crystallized from benzene in yellowish-white needles and melted at 141° - 142° . A nitrogen determination gave :

	Calculated for $C_{20}H_{15}ON_2S$.	Found.
Nitrogen.....	8.38	8.50

Benzylphenylparatolylamidine and Thiobenzoic Acid (by

Bayard Barnes).—The amidine was prepared from benzanimide-imide chloride and paratoluidine. On mixing this in benzene with thiobenzoic acid a pale yellow precipitate separated, melting at 131° – 132° . A nitrogen determination gave :

	Calculated for $C_9H_{14}ON_2S$.	Found.
Nitrogen.....	6.60	6.68

This compound did not decompose as smoothly, on heating, as that in the case of diphenylformamidine. The yellow product soluble in alkali as well as that which was insoluble was a mixture. In all probability both thiobenzanimide and thiobenztoluide were formed.

Benzimidonormalpropylester and Thiobenzoic Acid (by William Valentine).—Thirty grams of the imido ester were treated with 25.5 grams of thiobenzoic acid at 0° . A solid separated and on allowing the mixture to warm a little the solid melted and a reaction took place with the formation of a precipitate. This weighed 18.5 grams and it crystallized from alcohol in tablets which melted at 128° . A nitrogen determination gave 11.5 per cent. of nitrogen, while the calculated for *benzamide* is 11.5 per cent.

The oil removed from the above weighed 36 grams. It was taken up in ether, shaken with dilute alkali, washed, dried, and distilled at 16 mm. pressure. The portion boiling at 130° – 150° was distilled at ordinary pressure whereupon the larger portion boiled at 251° – 255° , a little distilling above 255° . A sulphur determination in the former agreed with the calculated for *n-propylthiolbenzoate*, $C_6H_5CO.SC_2H_5$.

	Calculated for $C_{10}H_{12}OS$.	Found.
Sulphur	17.8	17.6

Phenylacetimidomethyl ester and Thiobenzoic Acid (by William Valentine).—Twenty-five grams of the ester and 24 grams of thiobenzoic acid reacted immediately. The solid material that separated weighed 15 grams, it was crystallized from alcohol whereupon it melted at 154° – 155° and a nitrogen determination agreed with the calculated for *phenylacetamide*, $C_6H_5CH_2CONH_2$:

	Calculated for C_8H_9ON .	Found.
Nitrogen.....	10.37	10.37

The oil from the above contained benzyl cyanide and was not obtained in a pure condition.

Acetonephenylhydrazone and Thiobenzoic Acid (by William Valentine).—Thirty grams of the hydrazone and 28 grams of thiobenzoic acid were warmed for a number of hours on the steam-bath, whereupon some solid material (22 grams) separated and the loss in weight was about 1 gram. The solid material crystallized from alcohol in small prisms and melted at 168°–169° and a nitrogen determination agreed with the calculated for *benzoylphenylhydrazine*.

	Calculated for $C_{12}H_{19}ON_2$.	Found.
Nitrogen	13.1	13.0

On adding ether to the oil filtered from the above about 2 grams of solid material separated which, on crystallizing from alcohol, melted at 176°–177° and contained no sulphur. A nitrogen determination agreed with the calculated for *dibenzoylphenylhydrazine*.

	Calculated for $C_{20}H_{16}O_2N_2$.	Found.
Nitrogen	8.8	8.8

The ether solution of the oil was shaken with soda and then with dilute hydrochloric acid, whereupon about 10 grams of unaltered hydrazone were obtained. The remaining oil decomposed on attempting to purify it by distilling at reduced pressure.

Methyl Alcohol and Thiobenzoic Acid.—Ten grams of thiobenzoic acid and 25 cc. of methyl alcohol were boiled for twenty hours. The alcoholic solution was then treated with water and a little sodium bicarbonate, whereupon 7 grams of methylbenzoate boiling at 198°–200° were obtained. Calculated yield, 9.9 grams. The action of thiobenzoic acid and phenol under the same conditions was much slower.

Diisobutylammoniumthiolbenzoate, $C_6H_5COSH \cdot HN(C_4H_9)_2$. —

When the calculated quantity of thiobenzoic acid was added to diisobutyl amine, cooled in a freezing-mixture, the material solidified to a crystalline mass, while only a very little hydrogen sulphide was evolved. On crystallizing the material twice from alcohol it formed beautiful colorless flattened prisms which melted in a closed tube at 124°. A nitrogen determination gave:

	Calculated for $C_{15}H_{28}ONS$.	Found.
Nitrogen	5.24	5.43

This salt dissolved in water, and silver nitrate gave a pure white precipitate which blackened on boiling.

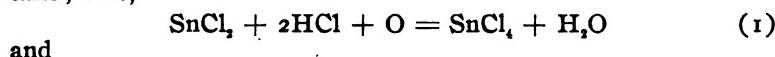
STUDIES ON SOLUTIONS OF STANNOUS SALTS, III.

BY S. W. YOUNG.

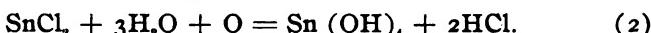
Received April 4, 1901.

PART I. THE COURSE OF THE REACTION BETWEEN STANNOUS CHLORIDE AND OXYGEN.

In a previous paper¹ it was pointed out that there were two probable courses which the reaction between stannous chloride and free oxygen, in presence of hydrochloric acid, might take; *viz.*,



and



It was also suggested that it might be possible to determine which of the two reactions was the one actually occurring, since if stannic chloride were first formed it would afterward slowly hydrolyze and thereby, on account of the formation of free hydrochloric acid in the solution, one would observe a gradual increase in the conductivity of the solution for some time after the oxidation was complete. Among others Kohlrausch² has recently investigated the change of conductivity with the time, in freshly prepared solutions of stannic chloride, and found that for dilute solutions, the increase was quite noticeable, but lasted for only a comparatively short time, when the conductivity became practically constant. In stronger solutions (about half-normal) the increase in the conductivity was still perceptible after several days.

The following investigations were carried out in the hope of applying this phenomenon to the determination of the presence or absence of stannic chloride in freshly oxidized solutions of stannous chloride. In order that the results might be as conclusive as possible several oxidizing agents besides oxygen were investigated. Among these a somewhat special interest is attached to sodium hypochlorite, since Thomsen³ found that with this oxidizing agent he obtained a very constant value for the heat of oxidation of stannous chloride, whereas with chlorine the values obtained were very irregular. One might surmise from this that the course of the oxidation was somewhat different in the two cases.

¹ This Journal, 23.

² Ztschr. phys. Chem., 33, 257.

³ "Thermochemische Untersuchungen," II, 445.

The results of the research are classified as to the oxidizing agent used. The general method was to oxidize the solution as rapidly as possible, transfer it to a conductivity flask and begin measurements as soon as the solution had acquired the temperature of the thermostat. The solution for oxidation was freshly prepared for each experiment. The hydrochloric acid concentration was varied in different experiments for reasons which will appear. The concentration of the stannous chloride was the same in all experiments, *viz.*, 2 grams of the crystallized salt in 100 cc., *i. e.*, about 0.16 normal. (Titration gave results as follows: 0.1625, 0.1623, 0.1630.)

All measurements were made in a thermostat at 25° C. The results cannot be used as a measure of isothermal reaction velocity, because, on account of lack of proper facilities, it was necessary to allow the thermostat to cool down each night.

I. OXIDATION BY MEANS OF FREE OXYGEN.

Solutions 0.1, 0.2, 0.3, 0.4, and 0.5 normal in hydrochloric acid were investigated. Since the oxidation ordinarily goes very slowly, all oxidations with free oxygen were accelerated by means of small quantities of hydrogen sulphide.¹ The time required for oxidation was from five to fifteen minutes, according to the acid contents of the solution.

Following are the tabulated results of the measurements with free oxygen. T is time in hours and K is specified conductivity in reciprocal ohms.

A. MEASUREMENTS WITH 0.1 NORMAL HCl.

1.	²	T = 0 1/6 2 4 19 21	K = 0.05999 0.06071 0.06159 0.06210 0.06247 0.06285
2.		T = 0 1/12 1/6 1/2 1 3 5 1/2 24 1/2 T = 62 105 125 K = 0.0880 0.0880 0.0880	K = 0.0797 0.0813 0.0818 0.0824 0.0837 0.0845 0.0853 0.0869

B. MEASUREMENTS WITH 0.2 NORMAL HCl.

1.	T = 0 1/6 4 1/2 6 23 1/2 25 1/2 K = 0.1140 0.1165 0.1180 0.1192 0.1192 0.1195
2.	T = 0 14 1/2 19 1/2 24 68 1/2 92 K = 0.1123 0.1168 0.1212 0.1220 0.1223 0.1223

¹ This Journal, 23, 144.

² In this experiment only 1 gram of stannous chloride per 100 cc. was used. In all others 2 grams were used.

C. MEASUREMENTS WITH 0.3 NORMAL HCl.

I.	T = 0	1/6	22 1/2	28	47 1/2	97 1/2	120	142
	K = 0.1010	0.1297	0.1523	0.1530	0.1540	0.1544	0.1544	0.1544

D. MEASUREMENTS WITH 0.4 NORMAL HCl.

I.	T = 0	1/12	1/6	1/4	1/3	1/2	3
	K = 0.1313	0.1390	0.1405	0.1423	0.1433	0.1464	0.1625
	T = 4	4 1/2	18 1/2	21	72	120	
	K = 0.1661	0.1670	0.1783	0.1802	0.1818	0.1838	

E. MEASUREMENTS WITH 0.5 NORMAL HCl.

I.	T = 0	1/6	1/2	23	28 1/2	48
	K = 0.1454	0.1460	0.1850	0.1910	0.1967	0.2064
	T = 72 1/2	97 1/2	120	143		
	K = 0.2110	0.2132	0.2160	0.2175		

From a consideration of the above results, it is apparent that in all cases there is an increase in the conductivity of these solutions with the time. Further, this increase is greater for solutions more concentrated in hydrochloric than for those less concentrated. This increase is very rapid at first, but its rate rapidly lessens. Thus it will be seen that a difference of a few minutes in the manipulation at the start makes a very considerable difference with the value of the total increase observed, but will have but little influence upon the total time required for the conductivity to become constant. Thus the greater length of time required for attaining equilibrium is more characteristic for concentrated solutions than is the absolute value of the increase in conductivity. In most cases the latter value is also greater for concentrated than for dilute solutions. The phenomena on the whole correspond almost exactly to those observed by Kohlrausch¹ upon dilution of stannic chloride with water, and there can be little doubt but that the oxidation of stannous chloride by free oxygen leads primarily to the formation of stannic chloride which then hydrolyzes, more rapidly in dilute than in concentrated solution. Thus the surmise made in a previous paper² that the oxidation leads directly to the formation of stannic or metastannic acid is not confirmed.³

2. OXIDATION BY MEANS OF POTASSIUM BICHROMATE.

The method of operation in this case (as in all following ones) was to weigh out the stannous chloride, add a requisite amount of

¹ Loc. cit.

² Loc. cit., p. 133.

³ c. f. Thomsen: loc. cit.

hydrochloric acid, oxidize with the dissolved oxidizing agent (in this case potassium bichromate), and finally to bring the solution to required volume with water. It was then placed in the conductivity flasks, and measurements made as before. The specific conductivities in this case are naturally considerably less than when the solutions were oxidized with oxygen, on account of the conversion of hydrochloric acid to potassium and chromium chlorides.

F. MEASUREMENTS WITH 0.2 NORMAL HCl.

I.	T = 0	$\frac{1}{12}$	$\frac{1}{6}$	$\frac{1}{3}$	$\frac{1}{2}$	1	$1\frac{1}{2}$	$16\frac{1}{2}$	$20\frac{1}{2}$	24
	K = 0.0645	0.0650	0.0665	0.0665	0.0668	0.0674	0.0676	0.0698	0.0700	0.0702

G. MEASUREMENTS WITH 0.3 NORMAL HCl.

I.	T = 0	$\frac{1}{12}$	$\frac{1}{6}$	$\frac{1}{3}$	1	2	21	55		
	K = 0.0898	0.0923	0.0928	0.0943	0.0958	0.0969	0.1000	0.1011		
	T = 98	122								
	K = 0.1011	0.1011								

H. MEASUREMENTS WITH 0.5 NORMAL HCl.

I.	T = 0	$\frac{1}{12}$	$\frac{1}{6}$	$\frac{1}{3}$	$1\frac{1}{2}$	$20\frac{1}{2}$	$24\frac{1}{2}$			
	K = 0.1192	0.1222	0.1263	0.1303	0.1357	0.1547	0.1552			
	T = 54	97	122							
	K = 0.1585	0.1585	0.1585							

3. OXIDATION BY MEANS OF FERRIC CHLORIDE.

Only one set of measurements was made with ferric chloride as oxidizing agent, and that with 0.1 normal hydrochloric acid as follows:

I. MEASUREMENTS WITH 0.1 NORMAL HCl.

I.	T = 0	$\frac{1}{12}$	$\frac{1}{6}$	$\frac{1}{3}$	$2\frac{1}{2}$	$4\frac{1}{4}$				
	K = 0.1053	0.1123	0.1153	0.1178	0.1327	0.1377				
	T = 24	28	61	104						
	K = 0.1515	0.1522	0.1570	0.1581						

It will be noticed that the increase here is very much more marked than in other experiments with 0.1 normal hydrochloric acid. The explanation lies very near, since the reaction between stannous chloride and ferric chloride is in itself a slow one.¹ The method of procedure was somewhat varied in this case in that the amount of a given ferric chloride solution necessary to oxidize the stannous solution was determined from preliminary experiments and this amount added to the solution under investiga-

¹ Noyes: *Ztschr. phys. Chem.*, 16, 546.

tion. The measurements show, however, an increase in the conductivity long after the reduction must have become complete, and the results for ferric chloride lead to the same conclusions as for other substances.

4. OXIDATION BY MEANS OF HYDROGEN PEROXIDE.

Three series of measurements were made with hydrogen peroxide, upon solutions respectively 0.1, 0.3, and 0.5 normal in hydrochloric acid. A somewhat special interest attaches to these experiments, since if the course of the oxidation with hydrogen peroxide showed itself to be different from that with free oxygen, we should have direct evidence that the oxidation by means of free oxygen was not brought about by the intermediate formation of hydrogen peroxide. As the results show, however, the course of the oxidation is the same with hydrogen peroxide as with free oxygen. Naturally this fact can in no way be taken as evidence that in the oxidation by free oxygen, hydrogen peroxide is an intermediate product. Following are the results of these measurements :

J. MEASUREMENTS WITH 0.1 NORMAL HCl.

T = 0	$\frac{1}{13}$	$\frac{1}{4}$	1	23	29 $\frac{1}{2}$
K = 0.0827	0.0837	0.0852	0.0881	0.0930	0.0932
T = 44	48	72 $\frac{1}{2}$	144	168	192
K = 0.0940	0.0943	0.0950	0.0958	0.0963	0.0963

K. MEASUREMENTS WITH 0.3 NORMAL HCl.

T = 0	$\frac{1}{13}$	$\frac{1}{4}$	$\frac{7}{12}$	1	3	6 $\frac{1}{2}$	20 $\frac{1}{2}$
K = 0.1223	0.1270	0.1311	0.1368	0.1395	0.1435	0.1527	0.1550
T = 25	49 $\frac{1}{2}$	122	146	170	194	218	
K = 0.1574	0.1583	0.1613	0.1616	0.1618	0.1622	0.1622	

L. MEASUREMENTS WITH 0.5 NORMAL HCl.

T = 0	$\frac{1}{4}$	$\frac{3}{4}$	$2\frac{1}{2}$	5 $\frac{1}{4}$	20	24
K = 0.1477	0.1503	0.1523	0.1595	0.1705	0.1883	0.1927
T = 49	122	146	170	194	218	290
K = 0.2045	0.2157	0.2190	0.2213	0.2224	0.2238	0.2253

5. OXIDATION BY MEANS OF SODIUM HYPOCHLORITE.

Two series of measurements were made with sodium hypochlorite, in solutions containing respectively 0.1 and 0.3 normal hydrochloric acid. The sodium hypochlorite was prepared by passing chlorine through cold dilute sodium hydroxide. As was mentioned at the beginning of this paper, some special interest

attaches to these measurements, since the heat of oxidation of stannous chloride by means of hypochlorite was found by Thomsen to give very definite results, while those with chlorine were quite variable. The results given below show, however, that hypochlorite forms no exception to the other reagents studied, in regard to the course of the reaction. Into a probable explanation of Thomsen's results upon the basis of these results, we will not at present enter.

M. MEASUREMENTS WITH 0.1 NORMAL HCl.

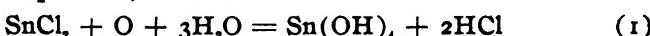
T = 0	$\frac{1}{12}$	$\frac{1}{6}$	$\frac{5}{12}$	1	$1\frac{1}{2}$	29	53	149
K = 0.1152	0.1180	0.1192	0.1216	0.1233	0.1243	0.1320	0.1326	0.1329

N. MEASUREMENTS WITH 0.3 NORMAL HCl.

T = 0	$\frac{1}{12}$	$\frac{1}{4}$	$\frac{1}{2}$	1	29
K = 0.1319	0.1338	0.1357	0.1386	0.1410	0.1710
T = 53	149	173	197	121	
K = 0.1766	0.1830	0.1838	0.1850		

SUMMARY OF RESULTS.

In all cases examined the freshly oxidized solutions of stannous chloride show electrical conductivities which increase with the time. This increase is in general greater for solutions more concentrated in hydrochloric acid than for those less concentrated. These phenomena are, to all appearances, identical with those noted by Kohlrausch,¹ and are, it seems to me, to be considered as giving indisputable evidence as to the course of the reaction between stannous chloride and the various oxidizing agents used. The conclusion to be drawn from these phenomena is that the first stage in the oxidation of stannous chloride is the formation of stannic chloride, and that for this purpose hydrochloric acid is necessary. In a previous paper² this question was taken up speculatively and certain evidence given which led to the surmise that the reaction took place in a somewhat different manner. As a result of the experimental evidence here given this surmise is shown to be wholly unfounded. The two equations given in the ordinary chemical nomenclature, expressing the two reactions in question, are as follows :



and



¹ Loc. cit.

² Loc. cit.

Reaction (2) is followed by :



The evidence shows distinctly that the reaction takes place according to (2) and (2a), which latter reaction is the cause of the increasing conductivity of the oxidized solutions with time.

The settling of this question adds one more case to those of reactions which follow the Ostwald rule¹ that "wherever an intermediate product can be formed during a reaction such product is formed," or in other words, the general tendency is for reactions to take place stepwise where possible.

The conclusion reached as a result of the preceding determinations is thus of fundamental importance in the correct formulation of the reaction-velocity in the case of the oxidation of stannous chloride with free oxygen. Part II of this paper will be devoted to a brief preliminary discussion of this point.

PART II. THE KINETICS OF THE REACTION BETWEEN STANNOUS CHLORIDE AND OXYGEN.

1. In a previous paper² the velocity coefficients for the reaction between stannous chloride and free oxygen in the presence of varying quantities of hydrochloric acid, were calculated upon the assumption that the hydrochloric acid did not enter directly into the reaction; *i. e.*, that its action was either catalytic, or else due to its influence upon the degree of hydrolysis of the stannous chloride. The values of the coefficients so calculated increased with the time in all cases. Since from the nature of the reaction the concentration of the hydrochloric acid must be greater at the end than at the beginning of the reaction, hydrolytic and catalytic influences could well explain the phenomenon. The catalytic explanation has the advantage over the hydrolytic one in that the phenomenon occurs in concentrations of hydrochloric acid so great that the hydrolysis of the stannous salt cannot well be considered to be very large. However, the results given in the first part of this paper show clearly that neither explanation is sufficient since the hydrochloric acid enters into the reaction as a definite reagent according to the laws of mass action, although it is, of course, by no means excluded that both catalytic and hydrolytic influences may also be at work.

2. Leaving hydrolytic and catalytic influences out of consider-

¹ *Ztschr. phys. Chem.*, 22, 307.

² This Journal, 23, 119.

ation for the present, and considering that the oxygen concentration is constant, we obtain as an expression for the reaction velocity the equation

$$\frac{dx}{dT} = K(A - x)^m(B - x + \Phi[x])^n, \quad (1)$$

where A is the initial concentration of stannous chloride, and B that of hydrochloric acid, and Φ is a function to be discussed later. For the exponents m and n we should set as most probable values, $m = 1$, $n = 2$, although it is not unlikely that $n = 1$.

3. The form of the function Φ is not determinable from any data at hand. Its value depends upon the rate of hydrolysis of stannic chloride in varying concentrations of hydrochloric acid. Kohlrausch¹ found that, in all probability, this reaction takes place according to a somewhat complicated law. For a somewhat simplified case, however, an expression for Φ is deducible. This case occurs when the primary reaction (the oxidation) is relatively slow, and the secondary one (the hydrolysis) very rapid. A low concentration of hydrochloric acid favors both conditions. In such an ideal limiting case $\Phi = 2$, since for each equivalent of hydrochloric acid used up, two are formed. Our equation then becomes

$$\frac{dx}{dT} = K(A - x)^m(B + x)^n. \quad (2)$$

By means of the integrated form of this equation I have calculated the velocity coefficients for the reaction in question, upon the assumption that $m = 1$ and $n =$ either 1 or 2 . In no case was a satisfactory set of values obtained, all series showing distinctly increasing or decreasing values of K with the time. The natural explanation is that the condition that $\Phi = 2$ is not sufficiently approximated.

4. Although the above equation (2) does not, for the reason just given, correctly formulate the reaction velocity in the case under consideration, there is, nevertheless, no reason theoretically, why reactions should not occur which would be correctly formulated by it, the sole condition being that the secondary reaction should occur at a rate relatively very large in comparison with the primary one. As a matter of fact the equation has been repeatedly used for the formulation of catalytic reactions in cases where one of the products is a catalyst; *e. g.*, the hydrolysis of

¹ *Loc. cit.*, p. 275.

methyl acetate.¹ In other words, from the standpoint of formulation, a catalytic reaction of the sort mentioned (hydrolysis of esters) and a reaction such as that under consideration are identical. Thus the reaction between stannous chloride, oxygen, and hydrochloric acid lends some experimental basis to the oft-made assumption that in catalytic reactions, the catalytic influence is, in many cases, due to the action of the catalytic agent in accordance with the laws of mass action, but in such a way that it is regenerated so rapidly that we fail to find evidence that it has gone into the reaction at all. Certain it is, at least, that if in the oxidation of stannous chloride, the subsequent hydrolysis of the stannic chloride were excessively rapid, we should naturally explain the whole influence of hydrochloric acid as catalytic.

5. From the foregoing it is seen that the equation (2) may be brought to apply to reactions in which it is not at all necessary to assume the presence of catalytic influences. Equation (2) may in all cases, with proper choice of A and B , show a maximum for $\frac{dx}{dT}$. Thus the statement made by Ostwald² to the effect that such maxima can only occur when catalytic influences are at work, is too broad. Such maxima are, from the foregoing, seen to be possible from a theoretical standpoint where catalytic action is excluded, and the results of the measurements given in a previous paper³ give ample experimental evidence of their existence in case of a reaction where, at present, it does not seem necessary to assume catalytic action.

6. The perfectly general form of equation (1) for several substances, $A_1, A_2, A_s, \dots B_1, B_2, B_s$, would be

$$\frac{dx}{dT} = K(A_1 - x)^{m_1}(A_2 - x)^{m_2}(A_s - x)^{m_s} \dots$$

$$(B_1 + \Phi_1[x])^{n_1}(B_2 + \Phi_2[x])^{n_2}(B_s + \Phi_s[x])^{n_s} \dots,$$

where A_1, A_2, A_s , are substances disappearing and not reappearing and B_1, B_2, B_s , are substances disappearing but reappearing as the result of secondary action in quantities greater than the quantities disappearing. Such an equation may have a considerable number of maxima and minima, as is determinable by simple algebraic considerations. Theoretically then a series of maxima are possible in a reaction running in two or more stages, when a sufficient num-

¹ See Ostwald: "Lehrbuch," II², p. 245.

² "Lehrbuch," II², p. 270.

³ Loc. cit.

ber of substances are taking part in such a way that the concentrations of some of them increase, and this without necessarily assuming catalytic influences. This would, of course, be equivalent to a "periodic" reaction in a homogeneous system. I know of no cases where such periodicity has been observed. It is quite possible that the well-known tendency toward simplicity of reaction may not allow such to occur. The theoretical point is mentioned here merely as a suggestion.

NOTE.

In the first paper of this series, measurements of the electrical conductivity of stannous chloride solutions are given and likewise of the influence of certain substances on the same. In the matter of the influences of potassium chloride upon the conductivity,¹ it was shown that the calculation was one of great uncertainty, so that a measure of the ability of potassium chloride to form complex salts in solution with stannous chloride was difficult to obtain. There is one phenomenon mentioned in that paper, however, which is capable of an interpretation, that, unfortunately, did not occur to me at the time of writing, and that is the marked and ever-recurring decrease in the values of $\frac{\Delta K \times 10^4}{C}$ with increase in C . This is just what would be expected if the association of potassium chloride with stannous chloride was very marked. For such cases we have the equation

$$\frac{(C_{\text{KCl}})^m \times (C_{\text{SnCl}_2})^n}{C_{(\text{KCl})_m} \cdot (\text{SnCl}_2)_n} = K.$$

If K is very small the first portions of stannous chloride will combine almost wholly with the potassium chloride in the solution, and a large reduction of the electrical conductivity will occur. This will be the result until a large portion of the potassium chloride has entered into combination, after which subsequent additions of stannous chloride will produce smaller and smaller decreases and ultimately an increase. This is noticed in the previous paper² very distinctly in the results for 0.25 normal potassium chloride and 0.5 normal hydrochloric acid, while the same general tendency is noted in all cases. It is, perhaps, unfortunate

¹ This Journal, 23, 32.

² Loc. cit.

that measurements with more dilute hydrochloric acid were not made, as in all probability the phenomenon would have been even more marked in such cases.

This is related here as a bit of evidence tending strongly to confirm the conclusion reached in the previous paper that potassium chloride exhibits a more marked tendency to the formation of complex compounds with stannous chloride in solution than does hydrochloric acid.

STANFORD UNIV., March 20, 1901.

THE REACTION BETWEEN CHLORINE AND AMMONIA.¹

BY WILLIAM A. NOYES AND ALBERT C. LYON.

Received May 17, 1901.

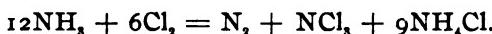
IN Hoffmann's well-known lecture experiment for the demonstration of the composition of ammonia, the introduction of the ammonia into the tube filled with chlorine, is followed by the addition of dilute sulphuric acid. Some years ago, when performing this experiment, it occurred to one of us that the use of the sulphuric acid was unnecessary, as any excess of ammonia would be absorbed by the large amount of water which is allowed to enter the tube later. The sulphuric acid was accordingly omitted, but with the surprising result that the tube was left only one-sixth full of nitrogen instead of one-third full, as it should have been. Recently an opportunity has been found to give the subject a more careful study.

A glass tube, having a capacity of about 95 cc. and closed at each end with a stop-cock, was prepared. This tube, after cleaning and drying, was filled with chlorine which was generated from manganese dioxide and hydrochloric acid and washed with water. The gas was passed through the tube from below till the portion escaping was completely absorbed by a solution of sodium hydroxide. After removing the chlorine from the tubes outside of the stop-cocks, aqua ammonia was allowed to enter the tube from above, and, after shaking gently, was followed by water till the residual gas was at atmospheric pressure. The amount of the nitrogen was then determined by filling the tube with water from a burette which was connected with its lower end.

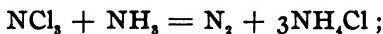
It was soon found that when strong ammonia is used in excess

¹ The work described in this paper forms the subject of a thesis by Mr. Lyon for the degree of Bachelor of Science at the Rose Polytechnic Institute.

the volume of the nitrogen is considerably greater than one-sixth of the volume of the chlorine, and may approach one-third of the volume of the chlorine but never reaches that limit. If, however, a solution containing 0.5 per cent of ammonia is used in such amount as to leave the solution faintly acid, the volume of the nitrogen approaches very closely to one-sixth the volume of the chlorine. If a 2 per cent. solution of ammonium chloride is used instead of the ammonia, the chlorine is almost completely absorbed and the volume of the nitrogen may be as low as only 1 or 2 per cent. of the volume of the chlorine. As will be shown below by quantitative results, the normal reaction between chlorine and ammonia is



This normal reaction is obtained, however, only when the ammonia is used very nearly in the proportion indicated. If an excess of ammonia is used, it reacts in part with the nitrogen trichloride, giving free nitrogen, in part, probably, giving ammonium hypochlorite.¹



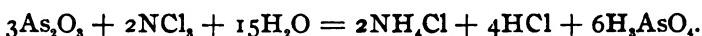
If, on the other hand, too little ammonia is used, the ammonium chloride formed by the reaction acts, in part, on the chlorine as stated above, with little or no evolution of nitrogen, and the volume of nitrogen liberated will be less than one-sixth the volume of the chlorine.

In studying the reaction quantitatively, the tube described above was covered with dark paper to prevent the action of light on the nitrogen trichloride formed. After filling the tube with chlorine an amount of 0.5 per cent. ammonia solution, equal to from 90 to 95 per cent. of that required by the reaction, was allowed to enter, the tube was shaken gently, and then water of the temperature of the original gas allowed to enter to atmospheric pressure. After gentle shaking a small additional amount of water would enter, indicating that an absorption of some kind had taken place, and the shaking was repeated till no more water would enter. Whether this small final absorption is due to residual chlorine, or to the fact that nitrogen trichloride has an appreciable vapor-pressure and is not quickly absorbed by the water,

¹ Schönbein: *J. prakt. Chem.*, 84, 386; Fresenius: *Ztschr. anal. Chem.*, 2, 59.

was not determined. The lower end of the tube was then connected with a burette and the amount of water required to fill the tube gave the volume of the residual nitrogen.

The contents of the tube were then transferred to a separatory funnel containing 10 cc. of benzene,¹ shaken, the benzene separated, and this repeated twice more. The benzene containing the nitrogen trichloride was shaken at once with an excess of a solution of arsenious oxide in sodium bicarbonate, and the excess of arsenious oxide determined with a standard iodine solution. The reaction is



Each atom of chlorine present is, therefore, equivalent to 2 atoms of "available chlorine."²

After titration the solution was distilled with an excess of caustic soda and the ammonia in the distillate was determined by means of a standard acid, thus proving that the substance extracted by the benzene was really nitrogen trichloride.

The solution which had been extracted with benzene, and which was, as has been explained, still slightly acid, was titrated with the same ammonia solution first used and the total ammonia required determined :

The results are as follows :

	Calculated.	I.	II.	Found. III.	IV.	V.
Volume of nitrogen as compared with chlorine	16.67	14.32	16.31	17.62	17.20	17.05
Available chlorine.....	50.0	49.3	43.4	35.7	45.5	41.7
Molecules of ammonia per atom of chlorine	1.0	0.97	1.03	1.04	1.01	0.98
Ammonia from NCl_3 . Mols. per mol of NCl_3	1.0	0.95	1.10	1.10	1.14	...

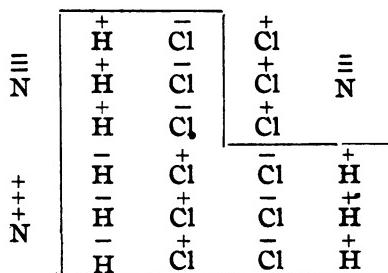
Owing to the instability of the nitrogen trichloride and to the secondary reactions which can never be entirely avoided, an exact agreement cannot be expected. The results satisfactorily demonstrate that the reaction already given is the primary one between ammonia and chlorine.

Probably the most interesting feature of the reaction here studied is the fact that 6 molecules of chlorine must react *simultaneously* with 3 molecules of ammonia, for, if the liberation of

¹ Hentschel : *Ber d. chem. Ges.*, 30, 1434.

² Hentschel : *Loc. cit.*

nitrogen by the action of 1 part of the chlorine were independent of the formation of nitrogen trichloride by another part, the constant relation of 1 volume of nitrogen to 6 volumes of chlorine would be improbable. The following hypothesis as to the cause of this relationship is given with some hesitation and in the hope that it may lead to discussion and to a further consideration of similar cases. If we suppose, what seems not inherently improbable, that all reactions involving the decomposition of molecules are preceded by an ionization of the parts of those molecules, it would follow that elementary molecules, as well, may ionize into positive and negative parts. This explanation of the reaction may be represented graphically thus :



The explanation given involves the further idea that in the ionization of ammonia the hydrogen may become either positive or negative. When we remember the neutral character of ammonia and the fact that its hydrogen may be replaced by either chlorine or sodium, such a thought is not so improbable as it seems when first presented.

That the hypothesis here suggested is capable of a wide application need hardly be said.

TERRE HAUTE, IND., May 15, 1901.

THE BOILING-POINT CURVE FOR MIXTURES OF ETHYL ALCOHOL AND WATER.

BY WILLIAM A. NOYES AND R. R. WARFEL.¹

Received June 5, 1901.

It has long been known that it is impossible to obtain absolute alcohol from dilute alcohol by distillation. Some years ago Le Bel² showed, also, that a 98 per cent. alcohol could be separated

¹ An account of the work here described was presented to the Faculty of the Rose Polytechnic Institute as a thesis for the Degree of Bachelor of Science.

² *Compt. rend.*, 88, 912.

by fractional distillation into an alcohol of 97.4 per cent. (by volume), and a residue containing 99.5 per cent. While these facts demonstrate that the boiling-point of absolute alcohol must be higher than that of alcohol slightly diluted, no one, so far as we can learn, has proved this by means of a direct determination.

The determination of the boiling-point curve for alcohol-water by J. K. Haywood,¹ has come to our notice since reading the proof of this article. Haywood entirely overlooked the minimum point. His curve, from alcohol of 85 per cent. down, agrees satisfactorily with ours.

The boiling-point apparatus of H. C. Jones² was used for the determinations. The tube of the condenser was sealed to the side tube of the apparatus, and was protected from the entrance of moisture at the top by means of a tube filled with calcium chloride. A small glass tube was inserted through the cork beside the thermometer, for the introduction of water or alcohol.

The alcohol used was rendered absolute by boiling twice with quicklime, the second time with the addition of a small amount of barium oxide. In distilling it, the first and last portions were rejected. The specific gravity of the alcohol indicated a strength of 99.98 per cent.

The boiling-points for alcohol from 100 per cent. to 64 per cent. were determined with a Beckmann thermometer graduated to $\frac{1}{100}^{\circ}$. Those from 64 per cent. to 0 per cent. were determined with a normal Green thermometer graduated in 0.1° . To determine the value of the degrees of the Beckmann thermometer the apparatus was connected with a large flask and a manometer, and the alcohol was boiled under diminished and also under increased pressure. In this way it was found that a difference of 1 mm. in pressure caused, at atmospheric pressure, a change of 0.0333° in the boiling-point. Ramsay³ and Young's tables give 0.0339° for 1 mm. The value of the degrees was, accordingly, taken as being sufficiently accurate for the present purpose.

To find the value of the Beckmann readings in terms of the true thermometer scale, pure water was placed in the apparatus, and it was connected with a large bottle and a manometer. The pressure was then reduced till the water boiled at about 80° of the true scale and a series of readings of thermometer, barometer,

¹ *J. Phys. Chem.*, 3, 318.

² *Am. Chem. J.*, 19, 581.

³ *J. Chem. Soc. (London)*, 47, 640.

and manometer were taken. The barometer and manometer readings were corrected to 0° and by comparison with Regnault's tables for the vapor-pressure of water, the point on the true thermometer corresponding to the readings of the Beckmann thermometer was determined. From this value the boiling-point of absolute alcohol under a pressure of 760 mm. is, as determined by us, 78.33° . The boiling-point calculated from the tables of Ramsay and Young¹ is 78.30° . As Ramsay and Young doubtless had much more accurate means than we could command for measuring heights of manometer and barometer, we have based our tables on their value for the boiling-point, instead of our own.

The barometer used was of the siphon form. The scale was compared with a standard scale by means of a dividing engine before it was filled, and the necessary correction applied. It was filled by ourselves, the mercury being boiled under diminished pressure during the filling.

In carrying out a series of determinations a weighed amount of alcohol or of water, or, in some cases of dilute alcohol, was put into the apparatus and the boiling-point determined. A weighed amount of water or alcohol was then added and the determination repeated. Each time, the barometer and its temperature were also read. The results were then corrected to a basis of 760 mm. by adding or subtracting $\frac{1}{30}^{\circ}$ for each 1 mm. difference in pressure. The nature of the readings will be apparent from the following illustration. In correcting the barometer readings a plus correction of 1 mm. for error of scale is included.

SERIES 7.

Grams of water added.	Barometer.	Temperature.	Barometer corrected to zero.	Beckman readings.	Beckmann readings cor- rected to 760 mm.	Per cent. of alcohol.
0.0000	737.6	19.5	736.13	2.948	3.744	99.98
0.2128	737.9	20.0	736.37	2.925	3.713	99.51
0.2440	737.95	20.0	736.42	2.907	3.693	98.97
0.1790	738.0	18.0	736.72	2.895	3.671	98.58
.....
.....
0.2900	743.5	17.5	742.28	3.089	3.680	92.42
0.2860	743.7	17.5	742.48	3.115	3.699	92.10

Started with 44.478 grams of alcohol of 99.98 per cent.

Six series of experiments, made before the use of the apparatus had been sufficiently mastered, were rejected. Four series

¹ Loc. cit.

which gave fairly concordant results were used to obtain mean values for the range from alcohol of 100 per cent. to 92 per cent. From these series the following values for each change of one-half per cent. in the amount of water were calculated by interpolation.

Per cent. of alcohol	7.	8.	10.	11.	Mean.
100.0	3.745	3.738	3.756	3.759	3.750
99.5	3.714	3.708	3.727	3.730	3.720
99.0	3.695	3.680	3.700	3.698	3.693
98.5	3.669	3.655	3.687	3.678	3.672
98.0	3.653	3.639	3.674	3.654	3.655
97.5	3.638	3.625	3.658	3.634	3.639
97.0	3.620	3.619	3.651	3.632	3.631
96.5	3.624	3.612	3.643	3.629	3.627
96.0	3.626	3.613	3.633	3.625	3.624
95.5	3.627	3.613	3.634	3.632	3.626
95.0	3.625	3.611	3.638	3.633	3.627
94.5	3.636	3.623	3.647	3.639	3.636
94.0	3.635	3.630	3.660	3.655	3.645
93.5	3.653	3.644	3.678	3.668	3.661
93.0	3.672	3.656	3.698	3.682	3.677
92.5	3.679	3.667	3.713	3.705	3.691
92.0	3.694	3.685	3.728	3.728	3.709

The remainder of the boiling-point curve possesses less interest and it was not attempted to secure the same degree of accuracy. From alcohol of 92 per cent. to 65 per cent. two series of determinations were made and the Beckmann thermometer was used.

For alcohol from 65 per cent. to 0 per cent., two series were made and the normal Green thermometer was used. As a part of the stem of the thermometer was outside of the apparatus a stem correction from the tables of Rimbach¹ was used. The correction for the thermometer at 100° was determined in the apparatus with pure water and the correction at 80° was determined by comparison with the Beckmann thermometer, whose value had been determined as described above. As the two corrections were different a table of corrections for intervening degrees was calculated on the supposition that the scale of the thermometer was uniform.

The final results of all the series are as follows:

¹ Ber. d. chem. Ges., 22, 3075.

Per cent. of alcohol.	Boiling- point.	Per cent. of alcohol.	Boiling- point.	Per cent. of alcohol.	Boiling- point.
100.0	78.300	88.0	78.445	55.0	81.77
99.5	78.270	87.0	78.530	48.0	82.43
99.0	78.243	86.0	78.575	37.0	83.76
98.5	78.222	85.0	78.645	35.0	83.87
98.0	78.205	84.0	78.723	29.0	84.86
97.5	78.191	83.0	78.806	26.0	85.41
97.0	78.181	82.0	78.879	22.0	86.11
96.5	78.179	81.0	78.968	20.0	87.32
96.0	78.174	80.0	79.050	18.0	87.92
95.5	78.176	79.0	79.133	13.0	90.02
95.0	78.177	78.0	79.214	10.0	91.80
94.5	78.186	77.0	79.354	8.0	93.10
94.0	78.195	76.0	79.404	7.0	93.73
93.5	78.211	75.0	79.505	5.50	94.84
93.0	78.227	73.0	79.683	4.50	95.63
92.5	78.241	71.0	78.862	3.0	97.11
92.0	78.259	69.0	80.042	2.0	98.05
91.0	78.270	67.0	80.237	1.50	98.55
90.0	78.323	65.0	80.438	1.00	98.95
89.0	78.385	63.0	80.642	0.50	99.65

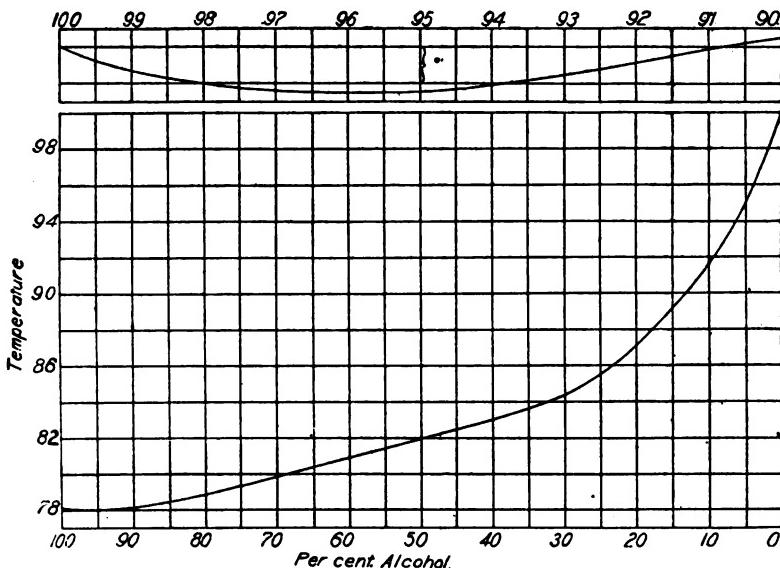
In the determination with small amounts of alcohol the readings of the thermometer were taken when the vapors first entered the condenser, as after boiling for a few minutes a relatively large proportion of the alcohol present would be found in the upper layers and in the condenser, and the thermometer under those conditions registered about 0.3 higher. It was shown by slow heating that the difference was not due to the lag of the thermometer.

An examination of the table and curve shows that the minimum boiling-point is for alcohol of 96 per cent. by weight. This corresponds to 97.45 per cent. by volume. Le Bel¹ gives the minimum as at 97 per cent. (presumably by volume, though he does not make this statement). His method would tend to place the minimum too low, unless moisture was very carefully excluded.

In the accompanying figure the upper part gives the boiling-point curve for alcohol of 90 to 100 per cent. on an enlarged scale. The lower portion of the figure gives the complete curve.

It will be seen that the curve is steeper on the side toward absolute alcohol than on the other side. Alcohol of 90.7 per cent. has the same boiling-point as absolute alcohol. An inspection of the curve also shows very clearly why it is easy to concentrate

¹ *Loc. cit.*



alcohol by distillation to a strength of 30 or 40 per cent. by weight, while the further concentration is relatively difficult.

Rose POLYTECHNIC INSTITUTE,
TERRE HAUTE, June 1, 1901.

THE VOLUMETRIC DETERMINATION OF ZINC.

BY PERCY H. WALKER.

Received May 15, 1901.

THE most commonly used method for the determination of zinc is the volumetric process of titrating with standard potassium ferrocyanide, using either a uranium solution or one of cobalt nitrate or platinum chloride as indicator. The ferrocyanide titration has several disadvantages. The standard solution does not keep well, and hence must be frequently standardized. If too much ferrocyanide is added in titrating, there is nothing to do but make another determination. The method of using an indicator, by taking out drops, invariably introduces an error.

R. K. Meade¹ has given us a method based on an entirely different reaction. He precipitates the zinc as zinc ammonium arsenate, and uses this arsenate to liberate iodine, which is then titrated by thiosulphate.

The most satisfactory gravimetric process for determining zinc is the precipitation of zinc ammonium phosphate and weighing

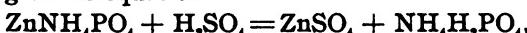
¹ This Journal, 22, 353 (1900).

as pyrophosphate, an analogous process being applied to manganese and magnesium.

Many years ago, Stolba¹ worked out an alkalimetric method for the determination of magnesium, by titrating the magnesium ammonium phosphate with standard acid. Handy's method² is a modification of Stolba's. This process may be much more easily used for the determination of zinc than for magnesium.

The process is carried out as follows: To the zinc solution, which should also contain ammonium chloride, a large excess of ammonia is added, then a large excess of sodium phosphate. The solution remains clear; but if the excess of ammonia is cautiously neutralized, a white cloud is formed as each drop of acid falls into the strong ammoniacal liquid. On stirring, this cloud dissolves until nearly all the ammonia is neutralized, when the whole solution becomes milky. It should now be heated to about 75° C. and stirred constantly, at the same time continuing the addition of dilute acid, drop by drop. In a very few minutes the precipitate becomes crystalline, and with care the liquid may be almost perfectly neutralized. It is a good plan to add a small piece of litmus paper to the liquid; this should not turn red but should remain blue or violet, while the hot liquid should have no odor, or only a very faint odor of ammonia. When the precipitation is made as above, the zinc ammonium phosphate is easily filtered, which may be safely done after five minutes' standing. The precipitate should be washed with cold water until the washings show only a faint trace of chlorides, then the paper with the precipitate returned to the beaker in which the precipitation was made, an excess of standard acid added, a few drops of methyl orange, and the exact point of neutrality determined with standard alkali.

According to the equation



we see that 1 cc. of normal acid corresponds to 32.7 mg. zinc. A solution of pure zinc oxide in hydrochloric acid was prepared for testing this method, the following results being obtained:

	Zinc taken. Gram.	Zinc found. Gram.
1.....	0.1490	0.1486
2.....	0.1490	0.1481
3.....	0.1490	0.1486

¹ *Chem. Centrbl.*, 1866, 727, 728; Sutton's "Volumetric Analysis," 6th ed., p. 87.

² This Journal, 22, 31 (1900).

Since the zinc ammonium phosphate is not precipitated in presence of a large excess of ammonia, the process may be used in the presence of magnesium which is precipitated in the strongly alkaline liquid, and the filtrate from the precipitate neutralized to precipitate the zinc. About 1.15 grams of crystallized magnesium sulphate were added to some of the zinc solution, made strongly alkaline with ammonia, sodium phosphate added, and after standing about fifteen minutes with frequent stirring, filtered, washed, and the zinc determined in the filtrate.

Zinc taken.	Zinc found.
0.1490	0.1481

The process gives fairly good results in the presence of iron, calcium, and magnesium, as the following results will show. Where unknown but rather large quantities of solutions of iron (ferric), calcium, and magnesium salts were added to the zinc solution, the whole being strongly alkaline, sodium phosphate was added in large excess, the solution being in a graduated flask which was filled to the mark, mixed, filtered through dry paper and an aliquot part taken for determining the zinc.

Zinc taken. Gram.	Zinc found. Gram.
0.1192	0.1172
0.1192	0.1172

Manganese, however, must be previously separated, best by the nitric acid and potassium chlorate method.

UNIVERSITY OF ARKANSAS, May 8, 1901.

THE EXTRACTION OF MORPHINE WITH IMMISCIBLE SOLVENTS.

BY W. A. PUCKNER.

Received June 11, 1901.

A recent publication by F. Wirthle¹ relative to the extraction of morphine from its solution by means of a chloroform alcohol mixture leads me to publish some similar determinations. My experiments were made with a view of ascertaining whether instead of liberating the alkaloid by addition of fixed alkali there might be substituted ammonium hydroxide. This work was not completed on account of similar determinations published by Kippenger². While I did not find the substitution of ammonia ad-

¹ *Chem. Ztg.*, 25, 291.

² *Ztschr. anal. Chem.*, 39, 290.

EXTRACTION OF MORPHINE.

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Shaken with 10, 10, and 10 cc. alcohol chloroform, the residue	Extracted with		Total morphine indicated by titration.
	a fourth 10cc. a fifth 10cc. the residue weighed.	Gram.	
10 cc. morphine solution (= 0.0008 gram alkaloid) was treated with	the titration indicated.	Gram.	Gram.
a ¹ 10 per cent. NH ₄ OH, 0.1 cc.	0.0988	0.0967	0.0010
a ¹ 10 per cent. NH ₄ OH, 0.1 cc.	0.0990	0.0983	0.0008
c ² 10 per cent. NH ₄ OH, 1.0 cc.	0.0937	0.0910	0.0054
c ² 10 per cent. NH ₄ OH, 1.0 cc.	0.0940	0.0919	0.0057
c ⁴ 10 per cent. NH ₄ OH, 1.0 cc.	0.0948	0.0922	0.0051
e ¹ NH ₄ OH, 1 cc., NH ₄ Cl, 3 grams....	0.0989	0.0856	0.0051
e ² NH ₄ OH, 1 cc., NH ₄ Cl, 3 grams....	0.0992	0.0847	0.0052
f ¹ 5 per cent. NaOH 0.2 cc.	0.0440
g ¹ 5 per cent. NaOH 2.0 cc.	0.0018
h ¹ 5 per cent. NaOH 0.2 cc. NaHCO ₃ , 1 gram..	0.0853	0.0147	0.0020
h ² 5 per cent. NaOH 0.2 cc. NaHCO ₃ , 1 gram..	0.0977	0.0952	0.0034
h ³ 5 per cent. NaOH 0.2 cc. NaHCO ₃ , 1 gram..	0.0991	0.971	0.0022
i ¹ NaOH 2 cc. NaHCO ₃ , 1 gram.....	0.0994	0.0974	0.0025
i ² NaOH 2 cc. NaHCO ₃ , 1 gram.....	0.0987	0.0023
j ¹ NaOH 2 cc. NaCl, 2 grams.....	0.0992	0.0071
k ¹ NH ₄ OH 1 cc., NaHCO ₃ , 1 gram.....	0.1008	0.0983	0.0008
k ² NH ₄ OH 1 cc., NaHCO ₃ , 1 gram.....	0.0997	0.0003

vantageous yet my results were more favorable than those of Wirthle and hence may be of some interest.

The morphine alkaloid used was purified by crystallization from hot absolute alcohol. Its purity, determined by titration with decinormal sulphuric acid and cochineal as indicator, was found to correspond to 99.50 per cent. monohydrated morphine ($C_{17}H_{19}NO_3 \cdot H_2O$). Of this, 2.5093 grams, corresponding to 2.4968 grams pure morphine, were dissolved in 10 cc. volumetric normal hydrochloric acid and sufficient water added to make 250 cc.

To extract and estimate the morphine in this solution 10 cc., representing 0.0998 gram morphine alkaloid, were in each case measured into a separatory funnel, rendered alkaline as below stated and then shaken with successive portions of a mixture composed of 80 volumes of chloroform and 20 volumes of alcohol. Three extractions of 10 cc. each were received in a shallow beaker (A). A further extraction of 10 cc. was received in a second beaker (B), and still another 10 cc. received in a third beaker (C). These liquids were allowed to evaporate spontaneously,¹ the residue kept over sulphuric acid for several hours, weighed, and then titrated with volumetric decinormal sulphuric acid, using cochineal as indicator.

These results show that while ammonium hydroxide combines with morphine to form a salt that is not readily taken up with the alcohol chloroform, it does so to a much smaller extent than sodium hydroxide. If as in *a* but a slight excess of ammonia is added, approximately 98 per cent. of the alkaloid is removed by the first three extractions. Even if ten times the amount used in *a* is added as in series *c* three extractions still remove more than 90 per cent., and practically all the alkaloid is obtained when five portions of the solvent are used. If a few drops of the cochineal indicator be added to the morphine solution and ammonia added to alkalinity the quantity used in *a* need not be exceeded. As might be expected the addition of sodium bicarbonate, *k*, overcomes the effect of an excess of ammonium hydroxide just as Kippenberger found this to be the case for fixed alkali. The

¹ If the evaporation is hastened by application of heat then a varnish-like residue is obtained from which the last traces of alcohol are expelled only with much difficulty. The residue left when the liquid has evaporated spontaneously is crystalline and loses no weight when dried at 60° C.; *i. e.*, morphine containing one molecule of water is thus obtained.

attempt to decrease the dissociation of the morphinate by ammonium chloride in ϵ and thus permit its removal from the solution did not prove successful. The ammonium chloride apparently acts as so much free ammonia. The discrepancy in ϵ between the weight of the residue and the morphine indicated by titration is due to ammonium chloride taken up by the solvent; to a moderate degree such disagreement is seen in all determinations.

UNIVERSITY OF ILLINOIS.

IMPROVED ELECTRIC FURNACE FOR LABORATORY USE.

BY SAMUEL AUCHMUTY TUCKER AND HERBERT R. MOODY.

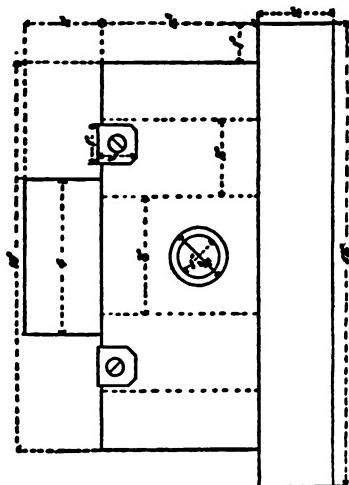
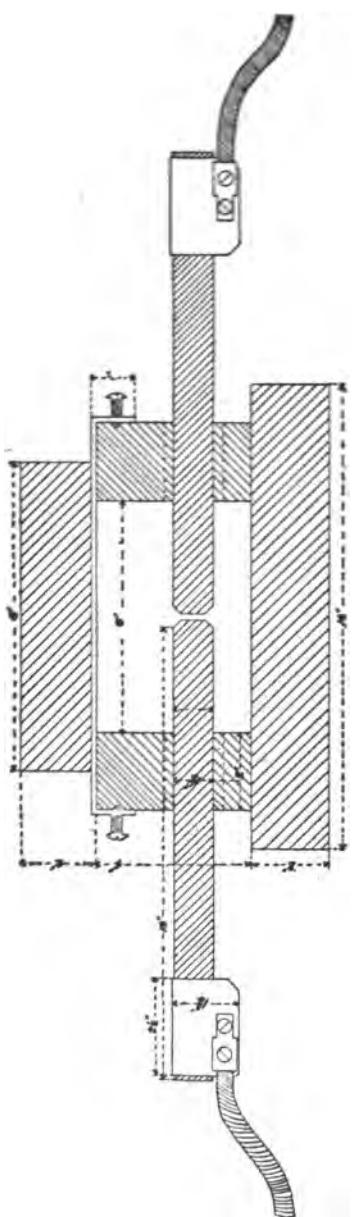
Received June 1, 1902.

ELECTRIC furnaces hitherto described have been found by the writers to possess certain disadvantages for experimental purposes. This led them to devise the form of furnace herein described which it is thought is a convenient piece of apparatus to build and will be found to be well adapted to a variety of work in the laboratory.

The Moissan type of furnace is now well known to every one, but it is troublesome in several ways. If built from chalk blocks in the rough, it takes both skill and time to cut them to the exact form required; it is then necessary to dry the blocks very thoroughly, otherwise they will crack in all directions and render the furnace useless immediately. A perfectly dry furnace supported by metallic bands will generally crack to some extent, and it is seldom possible to put the furnace in use a second time. The form of furnace described by one of us¹ which simply consists of a graphite crucible forming one pole, the other being a carbon rod supported vertically with an arrangement for raising and lowering it at will is useful for some purposes, but there is too much exposure to the air for many operations, and the material of which the crucible is composed is likely to introduce undesirable impurities during the fusion. The operator is exposed to very intense radiant heat which interferes considerably with its use for any lengthened period. The present form of furnace is after the Moissan type and is composed of carbon bricks 12 inches by 4 inches by 2 inches, luted together with Dixon stove paste. The sides of the furnace were of 6-inch brick, thus making

¹ American Electrician, 11, 408.

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a working space of about 6 by 4 by 2 inches. This space could, of course, be increased or diminished at will according to the charge used. The whole was then clamped and held firmly together by iron cross bars provided with adjusting screws at each end, these bars being insulated from the body of the furnace by strips of asbestos. The end bricks were perforated with 1.5-inch holes containing a collar of asbestos or a small cylinder of clay, through which the electrodes of carbon passed (1 inch by 12 inches) into the furnace chamber. Connection was made with these electrodes by copper sleeves lined with copper gauze and tightened with set screws which at the same time carried copper lugs which held the flexible cables.

The tendency to overheat those portions of these electrodes outside of the furnace, and consequent wasting away, and also the tendency to melt the copper connections, was overcome by either one of two expedients ; that is, by the use of the water-jacket or by heavily copper-plating the carbons. This latter did not furnish quite as perfect a protection, but it was somewhat less troublesome than the former, and was consequently the one most used.

The construction of this furnace gives it considerable durability; so much so is this the case, that only three sets of brick were used throughout the year in which almost a hundred runs were made. The greatest deterioration comes from the oxidation of the outer surface of the carbon bricks, and this could be largely avoided by a suitable covering of fire-bricks. Frequently ten or twelve runs could be made without dismantling the principal parts and the substitution of new asbestos collars serve to make everything ready for the next run.

In this type of furnace the desired current may be readily maintained throughout the entire fusion, and this is not easily done with a crucible furnace where variations are unknowingly introduced by the constantly changing distance between the poles. This form of furnace may be used with double arc on 110 volt circuit with considerable economy. For example, with a single arc furnace and with a polar separation of 18 mm. and enough resistance in circuit, the following reading was obtained : 125 amperes, 70 volts, and consequently 8,750 watts.

These should be compared with the following results obtained while using the double arc furnace. Here all the resistance was

cut out and then the instruments showed 175 amperes, and 90 volts. A few moments after this the reading was 125 amperes, and 100 volts or 12,500 watts.

The only difficulty in using this type is to prevent the extinction of the arcs, but that trouble is far from insurmountable. The dimensions given for the furnace are suitable for currents up to 300 amperes, at 70 volts. For work requiring more power than this it is necessary to increase the size throughout and use electrodes of 2-inch diameter.

If the luting has been carefully done the furnace will be sufficiently gas-tight to permit a fusion to be carried on in an atmosphere of any desired gas, the gas being introduced through an annular electrode. This furnace is adapted to almost all kinds of fusion processes, and has been used in the greatest variety of work.

[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL AND APPLIED CHEMISTRY, UNIVERSITY OF MICHIGAN.]

THE OXIDATION OF NITROGEN AS A SOURCE OF ERROR IN THE ESTIMATION OF HYDROGEN AND METHANE.

BY ALFRED H. WHITE.

Received June 20, 1901.

THE author had occasion some time ago to estimate accurately a small amount of methane mixed with a large amount of hydrogen. A sample mixed with air was exploded in a Hempel pipette with due precautions to insure accuracy, the measurements being made in the author's burette for exact gas analysis previously described in this Journal.¹ Though great care was taken in the work, the results were so discrepant as to be entirely useless for the purpose. The results of a series of five experiments follow, arranged in the order of explosive ratios.

TABLE I.—EXPLOSION OF HYDROGEN AND A SMALL AMOUNT OF METHANE.

Gas sample. cc.	Air. cc.	Contraction. cc.	CO ₂ . cc.	After explosion.			Explosive ratio.
				Hydrogen. Per cent.	Methane. Per cent.		
12.87	103.24	16.97	0.05	87.64	0.39	5.77	
13.79	86.89	18.39	0.04	88.51	0.29	5.08	
13.17	84.18	17.56	0.06	88.27	0.45	4.54	
14.77	87.23	19.66	0.09	87.92	0.62	4.20	
18.38	87.03	24.48	0.16	87.62	0.87	3.30	

The increasing amounts of carbon dioxide can not be laid to

¹ This Journal, 22, 343.

diffusion through the potassium hydroxide used, for the pipette carried enough mercury in the bottom to form a trap, nor to solution of gas by the potassium hydroxide, for the pipette had been carefully saturated by a blank experiment, nor to leak in connections because in each case after removing the carbon dioxide by potassium hydroxide, and reading the volume, the gas was passed back into the same potassium hydroxide pipette, allowed to stand and again drawn back into the burette and the volume read. In only one case, the third given, did the variation in volume after such second treatment with potassium hydroxide amount to as much as 0.02 cc. In two other cases, the variation was 0.01 cc. and in the other two there was no change in volume. Leaving out of account the first of the series where it is probable the great dilution caused incomplete combustion, the other four results show increasing methane and decreasing hydrogen as the explosive ratio (ratio of the inert to the exploding gas) grows smaller. The decrease in the percentage of hydrogen results from the method of calculation, all the contraction over potassium hydroxide being considered as carbon dioxide, and calculated to methane. The increase in the apparent carbon dioxide points strongly to the formation of oxides of nitrogen. That these are formed and may cause error in explosion analyses was shown long ago by Bunsen, who experimentally determined certain limits within which there was no appreciable error. The explosive ratio for pure hydrogen, according to Bunsen, might safely vary from 3.81 to 1.55. He did not determine whether any gases absorbable in potassium hydroxide were formed in the explosion. The results above cited have, with one exception, higher explosive ratios than his highest, and yet there is apparently considerable formation of an oxide of nitrogen which is absorbed by potassium hydroxide.

Bunsen's results have been seemingly everywhere accepted without question. Hempel, in the 1900 edition of his "Gasometrische Methoden," quotes Bunsen's results¹ with the comment that "by keeping to the Bunsen norm the worst that may happen is that the mixture is not explosive. The combustion of nitrogen will certainly be avoided."

The marked disagreement of the results given by Bunsen and those of Table I made it desirable to make a series of experiments

¹ Hempel: "Gasometrische Methoden," 3te Auflage, p. 113.

on pure hydrogen. The hydrogen was generated by the action of potassium hydroxide on aluminum in order to obtain it free from the small amounts of hydrocarbons usually present in gas obtained by the action of an acid on a metal. The results are given in Table II.

TABLE II.—EXPLOSION OF PURE HYDROGEN.

Sample hydrogen. cc.	Air. cc.	Contraction after explo- sion.	Hydrogen. Per cent.	Contraction over potassium hydroxide.	Explo- sive ratio.	Bunsen's results recalculated.	
						Explosive ratio.	Hydrogen. Per cent.
11.35	84.80	16.90	99.26	0.00	4.64	3.81	99.92
12.11	85.57	18.08	99.53	0.00	4.37	2.90	99.56
14.19	84.27	21.27	99.92	0.00	3.62	2.29	99.84
16.77	85.77	25.13	99.90	0.01	3.06	1.95	100.04
16.54	82.64	24.76	99.80	0.01	3.00	1.55	100.15
18.19	83.22	27.29	100.01	0.01	2.71	1.25	100.72
21.10	83.28	31.74	100.28	0.00	2.29	1.04	103.14
27.04	83.86	40.80	100.59	0.11	1.73	0.37	105.06

Bunsen's results recalculated to permit direct comparison are appended. Bunsen held that the explosive ratio might vary from 3.81 to 1.55 without causing appreciable error, though the smaller ratio gives erroneous results according to his own figures.

These figures for the explosion of pure hydrogen in Table II do not show as great variations with change of explosive ratio as do the results in Table I of explosion of a gas carrying a small amount of methane mixed with a large amount of hydrogen. To determine if the methane caused the difference, a series of explosions of methane and air were made. The methane was made from methyl iodide and the zinc copper couple, and both gas and air were freed from carbon dioxide before use. Table III gives the results of this series.

TABLE III.—EXPLOSION OF METHANE.

Sample methane. cc.	Air. cc.	Contraction after explo- sion.	Carbon dioxide cc.	Methane. cc.	Hydrogen. Per cent.	Explosive ratio.	Ratio sample	
							contraction	sample
7.05	92.07	13.09	6.53	92.62	0.28	4.05		1.85
8.93	104.17	16.66	8.31	93.28	0.14	3.53		1.86
9.07	98.35	17.10	8.54	94.15	0.14	3.19		1.88
10.20	98.22	19.27	9.63	94.41	0.06	2.61		1.89

In these experiments the explosive ratios all lie within Bunsen's limits for methane of 4-2.7; still there is a variation of 1.6 per cent. in the apparent percentage of methane as calculated by the usual methods and a corresponding variation in the amount

of hydrogen. The precautions mentioned before were taken to prevent error from diffusion or solution in the potassium hydroxide pipette. In all these experiments the gases had been diluted with air and the preponderating inert gas was nitrogen. Several experiments were made with mixtures of hydrogen and methane to determine whether any more trustworthy results might be obtained, using oxygen alone in excess. The oxygen gas used was 96.5 per cent. pure. The results showed that the errors when using oxygen thus were rather greater than when using air in similar amount. In several cases, both when using oxygen and air, Griess' reagent for nitrites (naphthylamine hydrochloride and sulphanilic acid) was introduced into the pipette before explosion, with the result that a deep red color was always formed after explosion, proving the formation of nitrous acid.

The explanation of the discrepancies between the author's work and Bunsen's is probably to be sought for in the different forms of apparatus employed. Bunsen used a narrow eudiometer in which the propagation of the explosion and liberation of heat would be slower and the absorption of heat by the glass walls more rapid than in the nearly spherical Hempel pipette; hence the temperature of combustion would be less in Bunsen's work and there would be a smaller amount of oxides of nitrogen formed. In Bunsen's eudiometer also explosion took place under diminished pressure, while in the Hempel apparatus a considerable plus pressure was generated in the explosion. It follows that when working with the Hempel apparatus a greater amount of inert gas than Bunsen found necessary should be present. Apparently the most nearly correct results are obtained in the case of hydrogen when the ratio of the non-explosive to the explosive gases follows Bunsen's higher figure; *i. e.*, when the explosive ratio varies from 4 to 3. In no case will absolutely correct results be obtained, as probably in all cases of explosion under these conditions nitrogen is oxidized to some extent. In the case of methane the higher temperature of combustion causes greater errors and here also the higher explosive ratio given by Bunsen should be adhered to.

The method of Dennis and Hopkins,¹ in which the gas in contact with a glowing platinum spiral burns quietly in a current of

¹ This Journal, 21, 398.

oxygen and air, allows the use of a larger sample. It is moreover indorsed by Hempel in the following words:¹ "The advantage gained is that in the beginning, where the combustion might become too intense, there is always an excess of combustible gas, so that on the one hand no explosion can take place, and on the other none of the nitrogen can burn, as the combustion takes place at the beginning with an insufficient amount of oxygen, and towards the end when the combustion becomes complete, such high temperatures as are necessary for the combustion of nitrogen are not reached at all."

Some preliminary experiments having shown that it was by no means so certain that nitrogen might not burn under these conditions, tests were made on air with Griess' reagent for nitrites in the pipette, when it was found that a test for nitrites quickly developed after heating the wire. Table IV shows quantitatively the effect on the volume of air when the spiral is heated to redness. The air was freed from carbon dioxide and the samples were as nearly as might be 80 cc. each. While it was not possible to measure accurately the temperature of the wire, a comparison could be obtained by measuring the current heating it. A current of 4 amperes heated the wire to barely visible redness in the daylight and 5.35 amperes heated it to a white heat. The time was in each case two minutes.

TABLE IV.—EFFECT OF HEATING PLATINUM SPIRAL IN AIR.

Sample air. cc.	Current amperes.	Contraction after heating. cc.	Contraction after potassium hydroxide. cc.	Total contraction. cc.
80.90	4.0	0.01	0.00	0.01
82.51	4.55	0.04	0.02	0.06
80.99	4.6	0.03	0.03	0.06
81.22	4.65	0.04	0.01	0.05
81.70	4.8	0.04	0.10	0.14
81.88	5.0	0.11	0.10	0.21
83.10	5.1	0.08	0.17	0.25
80.49	5.3	0.06	0.18	0.24
80.67	5.35	0.12	0.18	0.30

It will be observed that the sum of the contraction after heating and after potassium hydroxide given in the last column increases quite regularly with increase in temperature, but that there is considerable irregularity in the ratios between the contraction after heating and the contraction after potassium hydroxide. It

¹ "Gasometrische Methoden," 3te Aufl., p. 123-124.

may be that the more or less complete condensation of the nitric acid formed, depending upon time, contact, and the amount of water present, is sufficient to account for it.

To afford a direct comparison between the explosion and combustion method, hydrogen generated from aluminum and caustic potash was stored in a gas-holder containing mercury and a little dilute caustic potash. The hydrogen was supposed to be pure but evidently contained a little air. The oxygen used was about 97 per cent. pure.

TABLE V.—COMPARISON OF EXPLOSION AND COMBUSTION METHODS
ON HYDROGEN.

Explosions with Air.

Sample hydrogen. cc.	Air. cc.	Contraction after explosion. cc.	Contraction over potassium hydroxide. cc.	Hydrogen. Per cent.	Explosive ratio.
15.32	85.34	22.71	0.04	98.82	3.43
18.15	82.39	26.93	0.06	98.91	2.73

Explosions with Oxygen.

Oxygen.	Air.	Contraction after explosion. cc.	Contraction over potassium hydroxide. cc.	Hydrogen. Per cent.	Explosive ratio.
14.82	93.51	22.04	0.02	99.14	3.91
16.48	82.18	24.51	0.02	99.15	3.02
20.58	80.09	30.60	0.03	99.12	2.29

Combustions by the Dennis and Hopkins Method.

Oxygen.	Air.	Contraction after explosion. cc.	Contraction over potassium hydroxide. cc.	Hydrogen. Per cent.	Oxygen in excess.
91.29	51.65	54.55	136.72	0.04	99.84
58.48	53.39	50.14	87.43	0.10	99.66
89.31	40.77	50.21	133.57	0.07	99.70

The results of the explosions with oxygen are slightly higher than those with air, show very little contraction over potassium hydroxide, and remarkably little variation with change in explosive ratio. The results with the Dennis and Hopkins method are about 0.6 per cent. higher than those obtained by explosion with oxygen. The variations in the individual results by this method may easily be accounted for by the intentional variation in the proportions of nitrogen and oxygen used, and the unavoidable differences in temperature of spiral and time of heating.

The question naturally arises, which of these methods is more reliable. That none of them are entirely correct is certain, for if nitrogen of the air is oxidized to an appreciable extent by a platinum spiral heated to dull redness, oxides of nitrogen must be formed in all combustions. This has been shown by Ilosvay¹ for

¹ *Bull. Soc. Chim.*, II, 737 (1889).

flames, even when the temperature of combustion was much reduced by dilution of the gas with carbon dioxide. The same author also found a slight formation of nitrous acid in the case of air burning in an atmosphere of illuminating gas, where a reducing atmosphere would always be present.

SUMMARY.

Oxides of nitrogen are always formed in explosion analysis in amount increasing with the violence of the explosion. The dilution recommended by Bunsen, when exploding in eudiometer tubes under reduced pressure, is not sufficient when working with the Hempel explosion pipette. If the explosive ratio is kept between four and three, the error is negligible in the technical analysis of gases almost entirely hydrogen. The presence of small amounts of methane increases the error and if large amounts of methane are present, the error may easily amount to a per cent. or more. The explosive ratio should be kept between four and three as in the case of hydrogen. The method of Dennis and Hopkins tends to give high results, and the errors may easily become of importance if care is not taken to avoid heating the spiral too hot and too long. Neither the explosion method nor any method involving active combustion can give strictly accurate results.

ANN ARBOR, MICHIGAN,
June, 1901.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE.]

NOTE ON SOME MODIFIED FORMS OF PHYSICO-CHEMICAL MEASURING APPARATUS.

BY ALLERTON S. CUSHMAN.

Received May 21, 1901.

a. A CONVENIENT ARRANGEMENT OF THE KOHLRAUSCH-OSTWALD CONDUCTIVITY CELL.

In working with the usual form of Kohlrausch-Ostwald conductivity cell the writer has experienced some difficulty in arranging the electrodes so that they may be easily adjusted at any required distance one from the other, while on the other hand, when once set to a position the constant for the cell may be depended upon. The growth of physico-chemical methods of investigation has been so sudden that the manufacturers of instruments of precision have not kept pace with the requirements of

modern research. The physical chemist therefore has been obliged to depend largely on "home-made," and too often very imperfect, apparatus. It is not uncommon in many laboratories to see this important and delicate measuring instrument arranged in such a way that the electrodes are most insecurely fastened into place by means of splashes of sealing-wax, or, as is the case with the cells ordinarily supplied by the dealers, the mere friction of the glass supports of the electrodes against the holes in the ebonite cover through which they pass, is depended upon to insure the constancy of the cell.

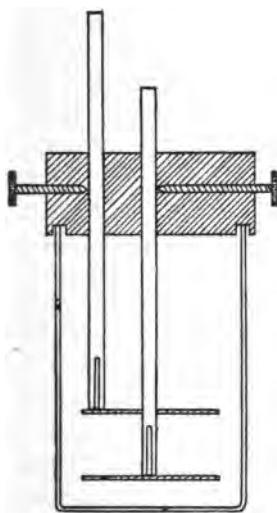


Fig. 1.

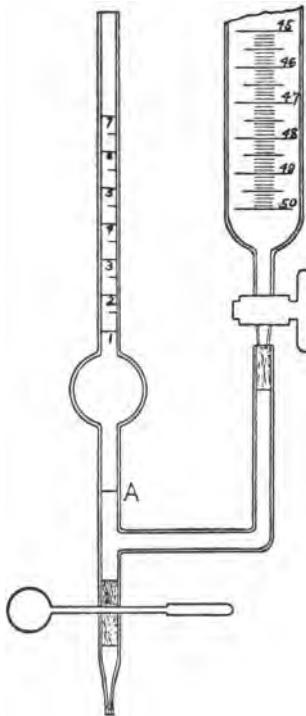


Fig. 2.

In Fig. 1 of the accompanying illustration is shown an arrangement of the cell which very admirably meets every requirement. The glass tubes into which the electrodes are fused, fit snugly, but without binding, the holes in the heavy ebonite cover, which is in cross-section in the cut. The brass set-screws as shown are

furnished with ebonite tips, which bear gently on the glass supports and remove the danger of contamination of the electrolyte by any accidental wetting of the screw points. A cell of this description which has been in frequent use for more than a year has not changed its constant. The electrodes are made of platinum, of nearly a millimeter in thickness and are secured to the glass supports with such care that they are quite immovable.

b. ON A MODIFIED FORM OF THE OSTWALD BURETTE-CALIBRATOR.

The usual Ostwald burette-calibrator has the general form shown in Fig. 2, without the etched scale upon the pipette stem. It is calibrated to deliver exactly 2 cc. between two etched marks and the deviations of the burette scale from the truth are then found by a series of deliveries from the pipette. The initial standardization of the pipette requires a number of careful and difficult weighings of water. In order to avoid this standardization the writer has used a pipette with a scale etched upon the stem as shown in the cut. It is only necessary to take care that when the pipette is filled to the etched mark at A that about 2 cc. more will put the meniscus somewhere near the middle of the pipette scale. Starting with the burette filled to the zero reading and the lower meniscus coinciding with the mark at A, the first 2 cc. of the burette scale are delivered into the pipette and the pipette-scale reading noted. The pipette is then emptied to A and the next 2 cc. of the burette delivered. This operation is repeated down the length of the burette. One set of readings can be made starting from the zero point of the burette and another set starting from the 1 cc. graduation mark. In order to apply the corrections it is only necessary to standardize the pipette scale against the burette scale by a few fractional fillings of the pipette. In applying the corrections any of the ordinary methods of calibration may be employed, such as assuming the first 2 cc. of the burette correct, and, then distributing the deviations from the truth. For most laboratory work exceedingly small deviations are negligible, but the fact that a serious deviation from the truth may introduce a constant error into a series of observations, makes a rapid and easy method of becoming acquainted with the variations of burette scales of great value. This instrument permits this to be done with but little expenditure of time and without the necessity of making a single weigh-

ing. Bad burettes can be immediately condemned and those of sufficient accuracy for the work in hand selected. In case absolute corrections are demanded the pipette can be standardized by the method of weighing much more easily than one that is not provided with an etched scale on the pipette stem. Of course the pipette must be made scrupulously clean with a chromic-sulphuric acid mixture before it is used.

May 20, 1901.

A RAPID METHOD FOR THE DETERMINATION OF ARSENIOUS OXIDE IN PARIS GREEN.

BY S. AVERY AND H. T. BEANS.

Received May 17, 1901.

THE authors have been working for some time on a method for determining the arsenic in Paris green, in the hope that one might be found that would be both more rapid and accurate than any thus far proposed. As a result we offer the following method, which we believe to be new and which has given most excellent results on a considerable number of samples of Paris green examined in this laboratory.

For the determination, sample the Paris green by quartering (as one would an ore for assaying) down to about 1 gram. Pulverize this small sample in an agate mortar and weigh out 0.2 to 0.3 gram into a beaker of about 300 cc. capacity. Add about 25 cc. of water and to the green suspended in water add, with constant stirring, concentrated hydrochloric acid till solution is just effected; from 6 to 10 drops are usually sufficient. Now add to the acid solution sodium carbonate solution till a slight permanent precipitate is formed, and at this point add 2 to 3 grams of sodium potassium tartrate in solution. The tartrate will at once dissolve the precipitated copper and prevent further precipitation during the subsequent titration. Dilute to about 200 cc., add solid sodium bicarbonate and starch solution, and titrate with iodine in the usual way.

The time required for the determination is about ten minutes. The end reaction is sharp and is not in the least obscured by the blue color of the copper solution.

TriPLICATE determinations on the same sample of a very uniform Paris green were as follows, taking 0.3 gram Paris green for analysis.

Iodine solution. cc.	As ₂ O ₃ . Gram.	As ₂ O ₃ . Per cent.
34.52	0.17056	56.85
34.59	0.17091	56.97
34.58	0.17086	56.95

To make sure that the presence of copper exerted no influence, several lots of pure arsenious oxide were weighed out. Some of these were titrated as usual and the others were first mixed with about an equal weight of copper sulphate in solution and then with the tartrate according to the method given. No appreciable difference could be observed in the several titrations.

Several other analysts, as well as ourselves, have found that the results, in terms of metallic arsenic, obtained by this method are slightly higher than the results by other methods, even when the latter admit of the determination of arsenic in either stage of oxidation. This fact would seem to indicate that the Paris greens on the market contain arsenic in the lower stage of oxidation only.

Cuprous oxide interferes with the titration, but we have not observed the presence of copper, in this degree of oxidation, in any of the samples examined. It is, of course, possible that adulterants might be added that would affect iodine or iodine salts, but such samples have not as yet been met with, to our knowledge.

In conclusion we would express our obligations to Dr. H. W. Wiley for his kindness in having the literature of the subject thoroughly searched for our guidance.

CHEMICAL LABORATORY, UNIVERSITY OF IDAHO.

NOTE ON THE ANALYSIS OF NUCLEIC ACIDS OBTAINED FROM DIFFERENT SOURCES.

BY P. A. LEVENE.

Received May 18, 1901.

THE author has repeated the results of the analysis of several nucleic and paranucleic acids obtained by a method communicated by him at a previous meeting of the Society.

The paranucleic acids analyzed were those of vitellin and of the ichtulin of the cod-fish egg. Their composition was as follows :

	Vitellinic acid.	Ichtilinic acid.
Carbon	32.31	32.56
Hydrogen	5.58	6.00
Nitrogen.....	13.13	14.00
Phosphorus	9.88	10.34

Thus these "paranucleic" acids of different origin have a comparatively similar composition. The difference in the nitrogen is easily explained by the fact that the ichtilinic acid was obtained from the ammonium salt, and the vitellinic from the copper salt. If the latter acid is obtained from the ammonium salt it also contains about 14 per cent. of nitrogen.

The nucleic acids analyzed were those of the pancreas of the cod-fish and fish sperm, and of the *Bacillus tuberculosis*.

Their composition was as follows :

	Pancreas.	Cod-fish sperm.	Bacillus tuberculosis.
Carbon.....	36.50	36.73	38.78
Hydrogen.....	4.69	5.12	6.32
Nitrogen	16.70	16.78	9.42
Phosphorus pentoxide ..	20.16	20.47	29.40

The acid obtained from the pancreas in distinction from the guanilic acid described by Bang contains in its molecule besides guanine also adenine. This acid as well as that of the cod-fish sperm does not differ much in its composition from the acids described within the last year by Schmideberg, Herlant, Osborne, and obtained from different sources.

The author also remarked that on precipitating the nucleic acids directly from tissues glycogen is precipitated simultaneously. The two can be separated by means of copper chloride. The nucleic acid forms a copper salt insoluble in water, while the copper compound of glycogen is soluble. By this method the author succeeded in obtaining glycogen from the pancreas, and a glycogen-like substance from the *Bacillus tuberculosis*.

ON THE ELIMINATION AND QUANTITATIVE ESTIMATION OF WATER IN OILS, FATS, AND WAXES.

BY CHARLES B. DAVIS.

Received March 19, 1901.

THE difficulty experienced while drying oils, fats, or waxes, (namely, loss by foaming and ejection, due to the contained water becoming overheated, as in the drying of the min-

eral oil residue obtained after removal of the fatty oil by saponification, in the analysis of lubricants) can be very readily obviated by the following method :

Into a wide-mouthed glass-stoppered weighing-bottle (see figure), is introduced sufficient thick filter-paper¹ (in coil form) to half fill the vessel. The bottle and paper are now dried in the air-oven at 110° C. to constant weight.



A portion of the sample is then added, in such quantity as will just saturate the filter-paper. The bottle being now closed and reweighed, the increase in weight gives the quantity of sample taken. The whole is now placed in the air-oven at 110° C.,² and dried to constant weight. The decrease thus obtained, gives the water evaporated, which may be calculated to percentage from the data obtained above. Samples prone to oxidation are dried in an atmosphere of CO, or H₂.

In treating oils containing water, or where the whole of the residue is to be dried and the oil only determined, or the water simply eliminated, the sample is completely transferred to the tared bottle containing the dry filter-paper by means of ether, the ether removed by evaporation at slightly elevated temperature, after which it is dried in the air-oven as above described.

Solid fats and waxes are introduced into the weighing bottle prepared as above, in their natural state, which, upon being warmed to the temperature of the oven, are quickly absorbed by the filter-paper, and drying proceeded with as in the case of liquids.³

By the above method, all foaming and ejection of the sample is eliminated, due to the fact that the oil, fat, or wax, and the water are thoroughly distributed throughout the paper while the drying operation is carried on.

A typical example of the value of the above method may be readily seen, and appreciated by referring to T. B. Stillman's "Engineering Chemistry," p. 368, in which he condemns the drying of oils containing water on account of this loss by foaming and ejection.

¹ Asbestos is not recommended on account of its property of retaining water even at 110° C. (this Journal, 22, 46).

² Or at temperature other than 110° C., in any case, the bottle, plus paper, is to be dried in the beginning at the same temperature.

³ If oil, fat, or wax be required for further examination, it may be removed from the paper by ether extraction in a Soxhlet apparatus.

ON THE DECOMPOSITION OF SODIUM NITRATE BY SULPHURIC ACID, II.

By C. W. VOLNEY.

Received May 24, 1901.

ON a former occasion¹ I presented to this Society a report on my work under the same title. The previous work had reference mainly to the conditions under which nitric acid distilled from a mixture of sodium nitrate and sulphuric acid.

Professor Lunge, in the second edition of his handbook "Sulphuric Acid and Alkali,"² quotes from the above cited article; but the process of decomposition in the said work, is still represented as $\text{NaNO}_3 + \text{H}_2\text{SO}_4 = \text{NaHSO}_4 + \text{HNO}_3$. I now report results of further investigation of this process. In the first part of the report already referred to, I have called attention to the strength of the nitric acid, which distilled at certain fixed temperatures, and I concluded, from the boiling-points, the temperatures of the residues in the retort, and the quality of the acid obtained, that during the second period all nitric acid had distilled off, and that only a disulphate was left in the retort.

I have since gone over the work again, and considered not only the distilled acid, but also the residues in the retort, which remain after each period of distillation. For this reexamination I used, for each period of distillation, a fresh quantity of nitrate and sulphuric acid, interrupting each process after the distillation of acid had entirely ceased, at the temperatures given. For each test, 500 grams sodium nitrate and 550 grams sulphuric acid were used; the results obtained were in agreement with those already described, as far as the strength of nitric acid is concerned. I have, at several times, attempted to separate the liquid from the solid portions of the salt cake. It is quite easy to separate the liquid from undecomposed nitrate by pouring the hot mass off. This must be done when the mass is still quite hot, as on cooling it will readily crystallize.

The distillation of nitric acid below 100° was carried out by heating in a liter retort, 500 grams sodium nitrate and 550 grams sulphuric acid at a temperature of 130° in the oil-bath, and keeping as near that temperature as possible, for thirty-six hours.

¹ This Journal, 13, 246.

² Edition of 1893, p. 116.

No further distillation could then be perceived. The residue in the retort consisted of unchanged nitrate and thick oily liquid. It was poured into a hot porcelain dish, which had been placed in an oil-bath of 100°, and from the hot mass a sufficient quantity of oily liquid was removed into another porcelain dish, where, on cooling, the liquid formed a crystalline salt in minute elongated prisms. The crystalline mass thus obtained, was left in a vacuum of 100 mm. at the ordinary temperature, for forty-eight hours, over sulphuric acid, and as it had lost nothing in weight, the sodium and sulphuric acid were determined, and gave the following results :

	Per cent.	Per cent.	Per cent.	Per cent.
Na	8.91	9.3	9.06	8.78
SO ₄	90.0	90.9	87.75	85.1

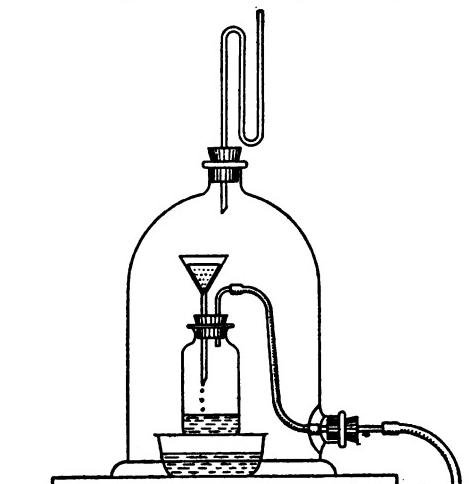
which gives on the average for this salt :

	Per cent.
Na	9.01
SO ₄	88.44

These results were obtained by the analysis of crystals furnished by solidifying the oily liquid above mentioned. As it is rather difficult to exclude the moisture of the air during the crystallization, and as thereby the crystals are destroyed, I have sep-

arated the solution from the solid residues in the retort, and then also from any possible excess of sulphuric acid, by filtration in vacuum, whereby the atmospheric air is almost totally excluded.

The simple apparatus is illustrated in the accompanying cut, and I may state here, also, that I arrived at the described construction of the apparatus after trying to obtain pure crys-



tals by centrifugal filtration and vacuum filtration in a Gooch cru-

cible ; but I prefer at present, the following apparatus : the glass funnel contains a filter of platinum, finely perforated, and it can be seen that only the air in the bell-jar, which is dried over sulphuric acid, can come in contact with the substance on the platinum filter. Under a vacuum of 650 mm. the solution of salts in sulphuric acid is quickly removed from crystals remaining on the platinum, and any absorption of moisture is excluded. The average of three determinations gave

Na	9.476
SO ₄	89.094

The sodium was determined as neutral sodium sulphate, and the sulphuric acid as barium sulphate. Comparing these with the composition of sodium trisulphate, NaH₃(SO₄)₂, we have the following :

	Calculated.	Found.
Na	10.550	9.362
SO ₄	88.07	89.147
H ₃	1.38	1.491
	100.000	100.000

The figures seem to be sufficiently close to the theoretical, to justify the conclusion, that during the first period of the action of sulphuric acid on sodium nitrate, the above indicated trisulphate is formed, provided that the temperature of the contents of the retort does not go above 100°. At this period then, the residue in the retort consists of the remaining sodium nitrate and sodium trisulphate. The process that has taken place, may therefore, be expressed by



and if the temperature is not raised above 100°, no further action of sulphuric acid on sodium nitrate can be perceived.

The second period of acid distillation ends at a temperature of 121°. For the investigation of this period, 500 grams sodium nitrate and 550 grams sulphuric acid were distilled in the same manner as before, but the temperature, after the first period of about 100°, was raised in the oil-bath to 165° and kept so, until all trace of acid, distilling at 121°-122°, had disappeared from the residue.

This was again poured hot into the heated porcelain dish, parts of the liquid cooled to crystallization, crystals dried in a desiccator over calcined potash at about 100 mm. pressure and finally sodium and sulphuric acid determined.

The figures obtained in these determinations are rather irregular ; they gave as an average

	Per cent.
Na	18.730
SO ₄	81.310

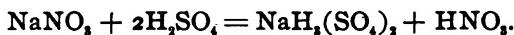
and compare with the acid sulphate of sodium thus :

	Calculated.	Found.
Na	19.166	18.730
SO ₄	80.000	81.310
H	0.834
	<hr/> 100.000	<hr/> 100.040

It is probable, that at the end of this phase some of the trisulphate, NaH₃(SO₄)₂, was still left in the residue ; but it seems reasonable to assume the existence of NaHSO₄ in the salt cake, which now remains in the retorts.

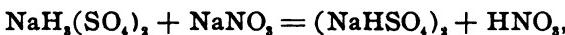
The conclusions, which may safely be drawn from this work, are :

During the first period of action of sulphuric acid on sodium nitrate, polysulphate of the composition NaH₃(SO₄)₂ is formed, thus :



The nitric acid, thus set free, is the true first hydrate and it distils over at its boiling-point between 81° and 88°.

The residue in the retort consists of trisulphate and nitrate, still undecomposed. On raising the temperature, the second phase of the process begins ; the trisulphate acts at the higher temperature on the remaining nitrate



and if this is carried out to the finish, the residue in the retort will consist entirely of NaHSO₄ ; and the acid distilling should also be HNO₃.

At the beginning of the distillation, free sulphuric acid is acting on a part only of the nitrate at a low temperature, at which the first hydrate distils undecomposed ; during the second period, the action of the trisulphate on the remaining sodium nitrate requires a higher temperature, at which nitric acid of the composition HNO₃ begins to decompose, and H₂O is always formed from HNO₃. The acid distilling during the period is, therefore, of a different concentration and is sometimes called the second hydrate. This investigation will be continued.

MODIFIED WILLIAMS METHOD FOR MANGANESE.

BY RANDOLPH BOLLING.

Received June 22, 1902.

THE Williams method, as outlined in Blair's "Chemical Analysis of Iron," although a very accurate one, is unsatisfactory on account of the time required for the filtration of the precipitated manganese dioxide, which, together with a frequently occurring mass of gelatinous silica, chokes up the asbestos filter and makes the operation more or less tedious.

The following modification has been found to overcome this difficulty entirely, and its adoption has reduced the time of a determination very materially, by eliminating the uncertainty attendant upon the filtration of the slimy manganese dioxide.

METHOD.

Place 5 grams of pig-iron drillings in a No. 5 Griffin's beaker, with cover glass, add 75 cc. nitric acid (sp. gr. 1.20), and after violent action has ceased add approximately 10 cc. hydrofluoric acid. Give the beaker a circular motion to mix contents, and evaporate down until ferric oxide begins to separate out. Cool, add 100 cc. nitric acid (sp. gr. 1.42), and heat to boiling. Drop in a spoonful of asbestos fibers and then add approximately 7 grams potassium chlorate. Boil until green fumes disappear and nitric acid begins to volatilize. Remove from source of heat, cool rapidly, and filter the manganese dioxide precipitated on the suspended asbestos fibers, on a special filtering tube. Wash twice with strong nitric acid, and rinse out the beaker in which the precipitation was made with cold water, pouring the rinsings through the filter-tube. Continue the rinsing and washing until, when tested with litmus, no acidity is shown. Push the asbestos pad and precipitate back into the beaker, wash down the sides of the filter-tube to remove all adherent manganese dioxide, and run in 50 cc. acid ferrous sulphate solution. Disintegrate the asbestos fibers with a stirring rod, and after the precipitate is entirely dissolved, titrate with permanganate. The filtering tube is prepared by taking a glass tube thin enough to slide loosely down the stem of a carbon funnel, heating one end until it balls and then pressing out flat. By softening the edge of the flat end and pressing a nail against the circumference at regular intervals the disk can be made fluted. Slip this rod in a carbon funnel, pushing down

until the disk rests solidly, place on it a little dry asbestos, and then pour on it asbestos suspended in water, using a moderate suction to make the pad fairly compact.

ACID FERROUS SULPHATE.

Dissolve 20 grams chemically pure ferrous sulphate in water, add 200 cc. strong sulphuric acid, and dilute to 2 liters.

POTASSIUM PERMANGANATE SOLUTION.

The strength of this solution should be such that 1 cc. equals about 0.0056 gram iron.

STANDARDIZATION AND CALCULATION OF RESULTS.

To standardize both the ferrous sulphate and the permanganate at the same time, take an iron in which the manganese has been accurately determined and treat it according to the method given until the precipitate of manganese dioxide is obtained. Dissolve the precipitate in 50 cc. of ferrous sulphate solution and titrate with permanganate, then run in 50 cc. additional of the ferrous sulphate and titrate again, to obtain the amount of permanganate necessary to oxidize 50 cc. of the ferrous sulphate solution. By deducting the number of cubic centimeters used in the first titration from the number used in the second, we obtain the volume of solution oxidized by the manganese dioxide. Dividing the percentage of manganese in the sample by the figure thus obtained and multiplying this by the number of grams of the original sample, we obtain the value of 1 cc. permanganate in terms of manganese. For instance, if we take 5 grams of a pig iron containing 1.13 per cent. manganese and use 4.6 cc. permanganate in the first titration, and 20.8 cc. in the second titration, then the difference of 16.2 cc. is the measure of the amount of ferrous sulphate oxidized by the manganese dioxide. Dividing 1.13 by this 16.2 and multiplying this by 5 we obtain the value of 1 cc. or 0.0034 gram manganese. The object of standardizing in this way, is to carry out the process under conditions similar to those which occur in a regular determination, for the results obtained by titrating clear ferrous sulphate are always lower than when carbon and asbestos are in the solution, for the reason that the eye of the observer notices the rose tint at once in a transparent solution, but the sharpness of the end reaction is slightly obscured by asbestos and carbon, hence the operator runs

a little past the true point. So that if both titrations are made under like conditions this error is completely eliminated.

The calculations in a determination are made thus : If 5 grams of the sample are taken, 50 cc. ferrous sulphate equals 20.8 cc. permanganate ; 1 cc. permanganate equals 0.0034 manganese ; 6.2 cc. are required to oxidize the ferrous sulphate not oxidized by the manganese dioxide.

$$\text{Then } \frac{(20.8 - 6.2) \times 0.0034 \times 100}{5} = \text{per cent. manganese.}$$

The time saved by the suspension of the manganese dioxide, and the elimination of silica in the filtering of the manganese dioxide, makes it possible to make a determination in about one hour. The method of standardizing solutions is not based on the reaction that is given in the text-books which is

$\text{MnO}_2 + 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 = \text{MnSO}_4 + \text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O}$, as it was found that solutions standardized on the above reaction were invariably too low in their manganese value. This may be accounted for in the composition of the precipitate, for it is possible that MnO , Mn_2O_3 , Mn_3O_4 , Mn_6O_7 , may be formed in part. At any rate, if we adopt the MnO_2 theory and standardize accordingly, the method will not give the same result on a sample that has the manganese determined by the basic acetate separation and the manganese weighed as manganese pyrophosphate according to Gibbs. On this account it is preferable to use a standardized sample of pig iron.

Below are given some determinations on ores and on some very carefully standardized pig iron.

Results in the first column are by using the Gibbs method.

In the second column by modified Williams method.

In the third by old Williams method, using the MnO_2 theory.

Sample No.	Percentage of manganese.		
	1	2	3
Iron ores.....	1.38	1.39	1.11
	1.84	1.84	1.51
	1.08	1.06	0.91
	1.34	1.35	1.20
	0.10	0.12	0.08
	2.87	2.87	2.14
	2.07	2.07	1.83
Pig iron	0.415	0.41	0.37
	0.442	0.44	0.38
	0.97	0.99	0.81

In working on ores carrying large amounts of silica it is advisable to dissolve the sample in hydrochloric acid and evaporate down to dryness, then moisten with hydrochloric acid and heat until the mass softens, and then add a few cubic centimeters of strong nitric acid; evaporate again until chlorine is driven out and then add hot water and filter off the silica and evaporate filtrate and determine manganese as usual.

I wish to acknowledge my thanks to Mr. W. Walley Davis, chief chemist, for his suggestions in regard to arranging the analytical data for publication.

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LABORATORY, ROANOKE, VA.

ON TRIVALENT CARBON.

(THIRD PAPER).¹

BY M. GOMBERG.

Received July 5, 1902.

IT has been shown in the papers published by me on this subject that by the action of metals upon triphenylchlormethane the halogen can be removed quantitatively and that there results an extremely unsaturated hydrocarbon. From the behavior of this substance towards halogens and towards oxygen, the conclusion was drawn that it is an unsaturated radicle, triphenylmethyl. It was shown that the same body results whether carbon disulphide, benzene, ether, or acetic ether is employed as a solvent. It was stated that in the case of the first two mentioned solvents the unsaturated hydrocarbon remains in solution, while with ether or acetic ester as a solvent the hydrocarbon separates in the form of large transparent crystals. This crystalline body possessed all the properties of the unsaturated hydrocarbon, and was also identical with the substance which was obtained when triphenylchlormethane in benzene was acted upon by zinc and the resulting hydrocarbon was precipitated from its concentrated solution by means of ether or acetic ester. Facts have since been discovered which necessitate a modification of this view, and I desire to publish the results even in their present incomplete state.

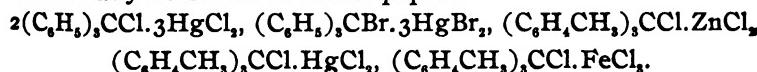
THE ACTION OF ZINC IN ETHER AS A SOLVENT.

When triphenylchlormethane is dissolved in absolute ether and a strip of zinc is introduced, the solution at once turns yellow and

¹ First paper: This Journal, 22, 757; Second paper: *Am. Chem. J.*, 25, 320.

a dark viscous mass begins to separate. After a while crystals begin to form which adhere to the zinc and to the sides of the vessel. If the reaction be carried on in a sealed tube it will be noticed that in a few days the black mass begins to diminish in quantity, and in about three weeks it will disappear completely. The solution still remains yellow but the crystals are colorless. It is impossible to get the ether and the reagents so absolutely free from moisture but that at least a few bubbles of hydrogen will be formed during the reaction.¹ The viscous mass which is formed at the beginning of the reaction is not zinc chloride, but a double salt of it with triphenylchlormethane.² Zinc chloride, I find, is soluble in ether, while the double salt is not. The thick yellow mass which was described under the experiments with benzene is also a double salt of a similar or of identical composition, and not a compound of zinc chloride with benzene, as has been previously supposed. Such a double salt when treated with water would give up all its chlorine to the latter, and this accounts for the somewhat misleading results which were obtained in the estimation of chlorine in the insoluble residue from benzene.³ On allowing the ethereal solution to stand for some weeks the double salt is completely broken up by the metallic zinc, but in benzene this does not occur. There is no separation of the double salt when acetic ether is employed as a solvent for the simple reason that the salt is very soluble in this solvent.

The same double salt is formed with the greatest readiness when a solution of zinc chloride in ether or in acetic ether is added to a solution of triphenylchlormethane in benzene or in absolute ether. All attempts to bring it to crystallization have failed, but a number of other double salts of triphenylhalogenmethanes, and especially of tritolylchlormethane, were obtained in sufficient purity to establish the remarkable tendency of these halogen bodies towards the formation of double compounds with metallic salts. Substances of the following composition were obtained, and they will be fully described in a later paper :



All these compounds are beautifully crystalline, and are charac-

¹ *Am. Chem. J.*, 25, 320.

² This Journal, 22, 761.

³ *Ibid.*, 22, 761.

terized by intense coloration, from yellow to red. There is no doubt that the yellow color which is imparted to the solution when zinc or any metal acts upon triphenylchlormethane is due in a large measure, but not entirely, to the formation of these double salts. The transparent yellow crystals which are formed when a solution of triphenylchlormethane in ether or in acetic ether is treated with zinc are not triphenylmethyl itself, but a compound of that with each of the two solvents respectively.

COMPOUND OF THE UNSATURATED HYDROCARBON WITH ETHER.

Samples of the above-mentioned yellow crystalline compound were analyzed from time to time, but the results usually fell from 2 to 3 per cent. short of 100 for the sum of carbon and hydrogen. This was at first ascribed to the absorption of oxygen by the unsaturated hydrocarbon during the washing and transference of the material. I then came back to the use of benzene as a solvent. An apparatus was constructed by means of which the benzene solution of the hydrocarbon could be concentrated in a vacuum at 30° C.; ether could then be added, and the crystals that were so formed could be filtered, washed, and thoroughly dried in an atmosphere of carbon dioxide,—all these operations being conducted in the same single piece of apparatus, without any rubber connections whatever. The crystalline product obtained in this way is almost insoluble in ether. It was washed with ether from fifteen to twenty times to insure the complete removal of the accompanying products such as triphenylmethane, triphenylcarbinol, etc. The crystals are at first perfectly colorless, but soon turn pale-yellow, the color increasing with standing. Twenty grams of triphenylchlormethane give about 7 grams of the insoluble crystalline compound. Molecular weight determinations of this substance were first made and the results were fairly satisfactory as calculated for triphenylmethyl.¹ An elementary analysis, however, gave the following results:

0.2884 gram substance gave 0.9488 gram carbon dioxide and 0.1900 gram water.

	Calculated for $(C_6H_5)_3C$.	Found.
Carbon	93.76	89.72
Hydrogen	6.24	7.37

¹ The determinations were made by the method of the lowering of the freezing-point, in an atmosphere of nitrogen, as carbon dioxide was found to be soluble in benzene to a sufficient degree to impair the results.

A fresh sample was then prepared in a similar way and was dried over sulphuric acid in a vacuum desiccator (previously filled with carbon dioxide) over night. It gave the following results : 0.2375 gram substance gave 0.7832 gram carbon dioxide and 0.1560 gram water.

	Per cent.
Carbon	89.94
Hydrogen	7.35

A new sample was then prepared, dried, and analyzed in the same day, but the results were almost the same.

0.2447 gram substance gave 0.8060 gram carbon dioxide and 0.1585 gram water.

	Per cent.
Carbon	89.83
Hydrogen	7.25

The next sample was prepared by the addition of a mixture of acetic ether and acetic acid instead of absolute ether, in order to hold better in solution any zinc salts which might possibly have accompanied the previously mentioned samples. This sample was washed first with acetic ether and then with absolute ether. It looked whiter and more distinctly crystalline than any before obtained, but the analysis gave figures for carbon and hydrogen, the sum of which was only 95.67 per cent. The close concordance of the first three samples, and the fact that when acetic ether, which carries almost twice as much oxygen as ethyl ether, is used for precipitating the hydrocarbon, a product proportionately richer in oxygen is obtained, suggested the idea that the substances analyzed must be compounds of the hydrocarbon with the solvents.

	Calculated for $2(C_6H_5)_3C + (C_2H_5)_2O$.	I.	Found.	III.
Carbon	89.93	89.72	89.94	89.83
Hydrogen	7.21	7.37	7.35	7.25

That we have here such a compound is proved by the following experiment : 0.9430 gram of the ether compound was placed in a platinum boat and gently heated at 70° C. in a tube, in a stream of carbon dioxide. The loss in weight was 0.1090 gram.

	Calculated for $2(C_6H_5)_3C + (C_2H_5)_2O$.	Found.
Loss	13.22	11.56

The escaping ether was easily identified by its odor, and a few droplets were also condensed in a small U-tube which was sealed on to the further end of the tube. The amorphous yellow residue

shows all the properties of the unsaturated hydrocarbon. It absorbs iodine with great eagerness ; a solution of it, when exposed to air, gives the triphenylmethyl peroxide. An analysis of the residue gave the following results :

0.1620 gram substance gave 0.5520 gram carbon dioxide and 0.1020 gram water.

	Calculated for $(C_6H_5)_3C$.	Found.
Carbon	93.76	92.93
Hydrogen	6.24	7.05

It remains yet to be settled whether this residue represents pure triphenylmethyl or a mixture of it with some of its decomposition products.

COMPOUND OF THE UNSATURATED HYDROCARBON WITH ACETIC ETHER.

A reaction entirely analogous to the one described above takes place when acetic ether is substituted for absolute ether. A compound of the unsaturated hydrocarbon with acetic ether is at once formed when triphenylchlormethane, dissolved in the ester, is treated with zinc. It is also produced when the metal is allowed to act upon the halogen compound dissolved in benzene, and to the concentrated solution acetic ether is added. The sample which furnished the results given below was prepared by the second method ; it was washed fifteen times with acetic ester, and was thoroughly dried in an atmosphere of carbon dioxide.

0.3160 gram substance gave 1.0180 gram carbon dioxide and 0.2080 gram water.

	Calculated for $2(C_6H_5)_3C + CH_3CO_2C_2H_5$.	Found.
Carbon	87.74	87.86
Hydrogen.....	6.69	7.37

The compound of the hydrocarbon with the ester is perfectly colorless when first prepared, but soon turns pale-yellow. It is more stable than the corresponding ether compound, and can be kept much longer without discoloration. It can be obtained in large crystals or in the form of a granular crystalline powder. On heating, it loses the ester.

1.1170 gram substance lost at 100° C. 0.1575 gram.

	Calculated for $2(C_6H_5)_3C + CH_3CO_2C_2H_5$.	Found.
Loss.....	15.50	14.10

The escaping acetic ester was condensed and identified as such.

The residue, after driving off the ester, looked like that obtained from the ether compound. It was amorphous, yellow, soluble in benzene and in carbon disulphide; it absorbed iodine and gave the peroxide. An analysis gave the following results:

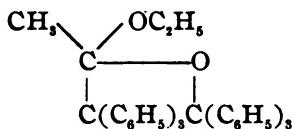
0.2135 gram substance gave 0.7250 gram carbon dioxide and 0.1322 gram water.

	Calculated for $(C_6H_5)_3C$.	Found.
Carbon	93.76	92.61
Hydrogen	6.24	6.93

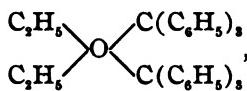
It will be noticed that in both instances the per cent. of carbon is somewhat low for triphenylmethyl. This may be accounted for by a slight oxidation, but I have no explanation at present as to the cause of the rather high per cent. of hydrogen.

WHAT IS THE NATURE OF THESE COMPOUNDS?

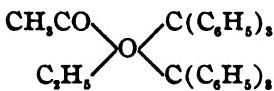
It is impossible to tell at this time whether in these two instances the ether and the acetic ester are those of crystallization or of constitution. Such a distinction is at best but an arbitrary one. One would expect that ether of crystallization would be easily driven off *in vacuo* over sulphuric acid,—which is not the case in this instance. From the extreme unsaturation of the hydrocarbon it may be assumed that it might add itself to acetic ester, giving a body something like this:



But it could hardly be expected that mere heating at 80°—100° C. would break up a chain of three carbon atoms in such a way as to regenerate the ester. Then, again, the combination with ethyl ether precludes any such addition theory in that instance. If it is not ether of crystallization, then the following constitution of that body suggests itself:



and the acetic ester compound may be supposed to have the corresponding constitution



In support of such a constitution might be cited the remarkable avidity of the hydrocarbon for oxygen, and the possibility of oxygen to act as tetravalent. Such a possibility was foreshadowed by van 't Hoff as long ago as 1877.¹ There has since been accumulating a considerable amount of evidence of physical nature pointing to such a possibility. In connection with this may be mentioned the recent work of Kanonnikow. From a study of alcohols and ethers at their critical condition, Kanonnikow² comes to the conclusion that in these compounds, under these conditions, the oxygen behaves as if it were tetravalent. The extreme unsaturation of triphenylmethyl presents an excellent opportunity to test the theory of the tetravalence of oxygen. The above formulas for the two compounds must be looked upon, at present, as a mere suggestion. It is my intention to extend this study to other oxygen compounds, as well as to nitrogen derivatives, and I beg to reserve this field for further work.

CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN,
June 29, 1901.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
No. 56.]

THE ATOMIC WEIGHT OF ANTIMONY.

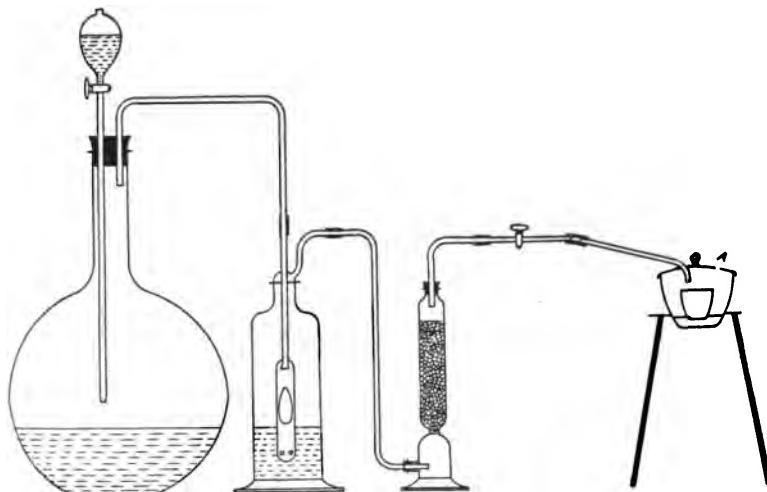
BY G. CLAUSEN FRIEND AND EDGAR F. SMITH.

Received June 8, 1901.

KNOWING that antimony oxide could be completely expelled from its combinations in a current of hydrochloric acid gas it appeared probable that a new ratio might be established for antimony, by exposing potassium antimonyl tartrate to the action of this gas. It will be recalled that by this procedure the atomic weights of molybdenum and arsenic had been previously determined in this laboratory. In these particular instances sodium molybdate and sodium pyroarsenate were exposed in porcelain boats, at a moderate heat, to the action of the gas, and from the weight of the residual sodium chloride the respective atomic weights were calculated. The method of work adopted with these metals was pursued with potassium antimonyl tartrate, but it was soon discovered that as carbon dioxide and water escaped the salt swelled up and was projected from the boat, so that a double crucible was substituted for the latter. On trial this de-

¹ "Ansichten über die organische Chemie."
J. Russ. phys. chem. Soc., 33, 197.

vice proved to be perfectly satisfactory, and it was possible in a crucible No. 00, from 1 to $1\frac{1}{2}$ inches in height, to operate with as much as 3 grams of material. The appended sketch represents the apparatus in detail.



A steady stream of hydrochloric acid gas was generated in the large flask by acting with pure, concentrated, sulphuric acid upon hydrochloric acid of like character. The gas was sufficiently dried by its passage through sulphuric acid and a column of calcium chloride and then introduced through a porcelain delivery tube into the crucible. The smaller crucible was supported in the larger one upon a perforated porcelain plate. The lid of the larger crucible had two openings, one for the entrance, and the other (A) for the exit of the excess of acid gas. Platinum crucibles should not be used; they are very severely attacked by the acid vapors.

In the experiments the dry gas was passed over the salt in the smaller crucible for half an hour, before any heat was applied. At the expiration of this period a small flame was placed under the crucible and it was heated to 150° for two hours, after which the temperature was gradually increased until the outer crucible showed a dull red color. This temperature was maintained until all of the volatile matter was expelled, when a stream of oxygen was substituted, for half an hour, for the acid. Most of the car-

bonaceous material was removed in this way, when the acid vapor was again introduced and the crucible contents allowed to cool in it. As the residual potassium chloride contained some carbon, it was dissolved in water and the solution filtered. The filtrate, with washings, was collected in a weighed platinum dish and evaporated upon a water-bath. The dish was supported upon a perforated glass plate. The dry potassium chloride was finally heated in an air-bath to 150° , then removed and gently heated over a flame to expel the last traces of moisture. On cooling, the salt was weighed. Two experiments made with potassium antimonyl tartrate, not especially purified, and with an ordinary balance and weights, gave the following results :

	Salt. Grams.	Potassium chloride. Grams.	Atomic weight of antimony.
1	2.0358	0.4691	120.44
2	2.5919	0.5973	120.41

This concordance in result and the ease with which the method could be executed, led us to prepare and purify large quantities of potassium antimonyl tartrate. To this end the purest commercial salt was recrystallized ten times, the first fraction only being used in each subsequent crystallization. The final 50 grams, intended for experiment, were dried at 150° for a period of sixteen hours. A weight was taken and the mass then again heated, cooled, and reweighed. There was no variation in the weight. This material was carefully tested for impurities (*e. g.*, arsenic, sodium, silica, etc.), and was found free from them. Portions of it were then acted upon as outlined in the preceding paragraphs.

The balance used in the subsequent experiments was constructed for atomic weight work by Troemner. It is sensitive to $\frac{1}{4}$ of a milligram with or without load. The weights of brass and platinum were carefully calibrated. All weighings were reduced to the vacuum standard. The specific gravity of potassium chloride was taken as 1.995 and that of the tartar emetic as 2.6 (Beilstein). The atomic weights used in the calculations were O = 16, H = 1.008, C = 12, K = 39.11, and Cl = 35.45. The results obtained with the pure material and with the observance of all the necessary precautions were :

	Potassium antimonyl tartrate. Grams.	Potassium chloride. Grams.	Atomic weight of antimony.
1	1.19481	0.27539	120.345
2	1.57004	0.36186	120.359
3	2.00912	0.46307	120.351
4	2.04253	0.47073	120.379
5	2.16646	0.49935	120.341
6	2.25558	0.51982	120.385
7	2.61255	0.60215	120.350
8	2.95272	0.68064	120.311
Mean = 120.353			
Maximum = 120.385			
Minimum = 120.311			
Difference 0.074			

The barium and silver antimonyl tartrates crystallize well and the hope was entertained that these salts might also be included in the circle of experimentation but thus far the results with them have not been satisfactory.

UNIVERSITY OF PENNSYLVANIA.

THE CHEMICAL NATURE OF ENZYMES.

BY P. A. LEVENE.

Received May 18, 1901.

There is comparatively little known about the chemical nature of the enzymes. In fact it is only in recent years that some attention has been given to these substances. Even the supposition that enzymes are of a proteid nature is not based on irrefutable evidence. Nevertheless, this is generally accepted. Very recently Hans Friedenthal claims that the enzymes possess the nature of nucleo-proteids.

It is chiefly in view of this last research that I have published some of the results of the investigation on the chemical nature of enzymes. The object of this work is to determine whether enzymes are actually of proteid nature. It was established during the last few years by the researches of Morochowetz, Lawrom, and Kutcher that proteids can be digested by means of trypsin to such an extent that the product no longer gives the biuret test, in other words the entire proteid material is decomposed. It was also demonstrated by Gulewitch that trypsin does not act on nitrogenous substances of non-proteid nature. Hence it seemed possible to test the proteid nature of enzymes by subjecting them to tryptic digestion.

The statement has, however, been made that some enzymes are destroyed even by a comparatively short digestion with trypsin, but this statement has also been contradicted. It therefore appeared advisable to repeat these experiments.

Popow has demonstrated that trypsin decomposes nucleoproteids, splitting off their phosphorus as phosphoric acid, and it seemed therefore possible to ascertain by means of tryptic digestion, whether enzymes were of the same nature as nucleoproteids.

I performed my first experiment in September, 1899. Several pounds of fresh pancreas glands were chopped, treated with 0.5 per cent. solution of sodium carbonate and a large quantity of chloroform. The mixture was allowed to stand over night. It was then strained through gauze and the liquid divided into several flasks, more chloroform added, and then placed in the thermostat at 40° C. The contents of the flasks were well shaken every day. After a couple of weeks of digestion the contents of the flasks were filtered, the filtrate transferred into acid bottles, a considerable quantity of chloroform added and placed in a very warm room. The bottles remained there until May, 1900.

The solution which was very dark in color, was then decolorized by means of animal charcoal, and tested for biuret and gave a negative result.

Another part of the same decolorized liquid was treated with a great excess of alcohol and the whole precipitate thus obtained tested for biuret without result.

From the above negative tests it was assumed that all the proteids of the original extract were decomposed. In order to test how far the decomposition of the nucleic acid went, a determination of the phosphorus in the form of organic and inorganic compounds was made.

In 25 cc. of the solution the phosphoric acid was precipitated by means of magnesia mixture. The precipitate slightly colored was redissolved with hydrochloric acid and reprecipitated with ammonia. The magnesium pyrophosphate weighed 0.257 gram.

Another 25 cc. of the same liquid was evaporated to dryness, and the residue fused with sodium carbonate and potassium nitrate. The phosphorus was estimated in the usual way. The magnesium pyrophosphate weighed 0.249 gram.

This experiment demonstrated that trypsin is able to decom-

pose absolutely the nucleo-compounds of the pancreas, as well as the proteids. This solution of the self-digested pancreas extract, however, has no proteolytic activity.

It was then attempted to subject trypsin to self-digestion for a shorter period, so as either to break up all the nucleins and leave some proteid material intact or vice versa.

Grubler's trypsin was used for these experiments. About 3 grams of the substance were treated with 150 cc. of 0.5 per cent. solution of sodium carbonate and allowed to stand six weeks. At the end of that time the mixture was filtered. The filtrate gave a positive though very weak biuret test, and possessed tryptic activity. 50 cc. of the solution were used for the estimation of the total phosphorus, another 50 cc. for the estimation of phosphorus in the form of phosphoric acid. The total phosphorus weighed 0.00125 gram and the phosphorus as phosphate weighed 0.0012, thus showing the absence of nucleo compounds in the solution, and still the solution contained the proteolytic enzyme.

In experiment No. 2, 30 grams of trypsin (Fairchild) were treated with 50 cc. of 0.5 per cent. solution of sodium carbonate (a great excess of chloroform added as an antiseptic), and allowed to stand in an incubator.

After three weeks of self-digestion part of the mixture was filtered and tested for proteolytic activity. The result was positive. In 25 cc. of the filtrate, the total phosphorus was estimated, and it weighed 0.0162 gram. In another 25 cc. portion the phosphorus is estimated as phosphate; it weighed 0.0131 gram, thus showing the presence of traces of nucleo-compounds.

After four weeks of self-digestion another experiment was made similar to the former. The solution still possessed its proteolytic properties. 10 cc. of it contained 0.00715 gram phosphorus. Another 10 cc. of the same contained 0.00628 gram phosphorus as phosphate, again showing the presence of a slight amount of nucleo-compounds.

The experiment was again repeated after six weeks of self-digestion. The solution was still active and gave the test for biuret. 10 cc. of the solution contained 0.00715 gram total phosphorus. 10 cc. of the same contained 0.00663 gram phosphorus as mineral phosphates, thus containing scarcely any nucleo-compounds and still possessing proteolytic activity. These experi-

ments would scarcely justify the conclusions of Freslenthal that trypsin is a nucleo-compound.

The fact that only those solutions were active which gave a positive biuret test would seem to indicate that trypsin is of a protein nature. However, in some cases the biuret test was scarcely perceptible, and yet the solution of the self-digested trypsin still contained the active ferment.

Experiments on other enzymes in the same direction are now in progress.

I wish to express my indebtedness to Doctor D. Sculley for the assistance received from him.

CONTRIBUTIONS TO THE KNOWLEDGE OF REVERSIBLE REACTIONS.

BY W. N. STULL.

Received June 17, 1901.

THE object of the study outlined in the following pages was primarily to investigate the positions of the points of equilibrium when acid solutions of certain metals were treated with hydrogen sulphide, and to determine the influence of agitation and temperature upon these points. Incidentally to this main purpose, it was thought desirable to ascertain under what conditions the separation of certain metals, such as zinc and cadmium, could most accurately be effected by hydrogen sulphide. The author has been unable to find any account of accurate determinations upon this latter point, though the common method of separating zinc and cadmium by hydrogen sulphide is practiced in almost all laboratories.

At the beginning it was found that the attainment of equilibrium with acid solutions of zinc and cadmium presented serious difficulties, since the reactions are exceedingly slow, and, in fact, in no case was complete equilibrium reached even after the solution had been treated with a rapid stream of hydrogen sulphide for many hours. As the work advanced, therefore, the importance of the speeds of the reactions became more and more apparent, and as a result this factor became the chief object of study, and incidental thereto, the effects of temperature and agitation.

Since the author must discontinue the work for a time to devote himself to other duties, it is deemed best to publish the results, incomplete as they are, on account of their bearing upon practi-

cal problems of analysis. At a later date he hopes to continue the work and discuss it with reference to the theory of equilibrium and mass action. Thus far the work has extended only to zinc and cadmium in hydrochloric and sulphuric acid solutions.

Apparatus and Precipitation.—The solution of the metal was contained in two tubes immersed in a water-bath, kept at constant temperature by a thermostat. Washed hydrogen sulphide was passed into the tubes at the rate of about 4 liters per hour. At the end of any period of time selected, a portion was filtered and the zinc or cadmium remaining in solution determined. The zinc was determined volumetrically by the ferrocyanide method of Lyte. Cadmium was determined as the sulphide. When temperatures higher than 30° were used a tube partially filled with water was placed in the bath and connected between the gas-generator and the precipitation tubes so as to compensate so far as possible for the loss of water from the solution by evaporation.

SERIES I. ZINC IN HYDROCHLORIC ACID SOLUTION.

Column I indicates the number of the determination, II the time in hours, III the per cent. of free hydrochloric acid, and IV the per cent. of zinc remaining in solution. The temperature was 20°.

I.	II.	III.	IV.
1	0.5	0.06	4.31
2	1.0	0.57	3.84
3	1.5	0.98	3.48
4	2.0	1.53	3.00
5	2.5	1.76	2.78
6	3.0	1.92	2.63
7	3.5	2.14	2.42
8	4.0	2.27	2.32
9	4.5	2.35	2.25
10	5.0	2.48	2.13
11	5.5	2.65	1.98
12	6.0	2.72	1.92
13	6.5	2.86	1.81
14	7.0	2.98	1.69
15	7.5	3.18	1.55

It will be observed that at the end of seven and one-half hours, precipitation was still taking place and at a rate which indicated that equilibrium was yet far removed.

SERIES II. ZINC IN SULPHURIC ACID SOLUTION.

The conditions of precipitation were the same as in Series I. Here, as in Series I, the zinc sulphide precipitated was perfectly white, the zinc used being a very pure specimen that showed no impurity save a trace of iron, and an amount of carbon residue too small for determination. Column II shows the time in hours, column III the per cent. of free sulphuric acid, and IV the amount of zinc remaining in solution.

I.	II.	III.	IV.
1	0	1.09	2.29
2	1	2.12	1.60
3	2	2.65	1.25
4	3	3.40	0.75
5	4	3.95	0.38
6	5	4.26	0.18
7	6	4.38	0.07
8	7	4.47	0.03

At the end of seven hours precipitation was still going on, although very nearly complete. The solution contained about 4.50 per cent. of free acid. In order the better to compare the restraining action of the two acids, it was thought desirable to use solutions which would contain approximately the same amounts of zinc at the beginning and at the end of the precipitation. The results are shown in Series III.

SERIES III. ZINC IN SULPHURIC ACID SOLUTION.

I.	II.	III.	IV.
1	1	0.95	4.24
2	2	1.76	3.68
3	3	2.28	3.35
4	4	2.88	2.94
5	5.5	3.49	2.54
6	6.5	3.77	2.35
7	7.5	4.18	2.08
8	9.0	4.61	1.80
9	10.5	5.25	1.37

The course of the reaction in the presence of free sulphuric acid is very similar to that in the presence of free hydrochloric acid. The curves representing time and precipitation in the two cases are very nearly parallel. Comparing the amounts of free acids at the end of equal times (seven and one-half hours) in Series I and III, it may be observed that sulphuric acid exerts little less re-

straining influence than hydrochloric, since the amount of the former exceeds the latter by only about 1 per cent.

Influence of Time.—It seemed desirable to determine the influence of time, if any, upon the amount of precipitation, and to this end four experiments were performed with the same solution. In the following table, column II gives the time during which the gas was passed into the solution, column III the time in hours that the solution was allowed to stand before filtering, IV the free hydrochloric acid, and V the zinc remaining in solution. In 3 the solution was shaken one and one-half hours before filtering. Of course the tubes were kept tightly stoppered while standing. At the ends of the respective times the solution still contained much free hydrogen sulphite.

SERIES IV.

I.	II.	III.	IV.	V.
1	1	0	2.82	1.83
2	2	12	3.11	1.57
3	1	13.5	3.10	1.57
4	3.5	13.5	3.87	0.89

The results show some precipitation after the hydrogen sulphide has been stopped, but probably a three-sided equilibrium of hydrogen sulphide, hydrochloric acid, and zinc chloride is reached within a few hours, and this does not seem to be affected by agitation.

Influence of Agitation.—In order to determine more fully the effect of agitation upon the rate of precipitation, portions of a solution containing 4.86 per cent. of free and combined hydrochloric acid were treated in two tubes, with hydrogen sulphide. In one of these tubes was a stirrer kept in rapid motion by a hot-air engine. The tubes were kept at the same temperature, 20°. Column V shows the amounts of zinc remaining in solution in the tube not provided with a stirrer, at the ends of the respective periods, and column IV gives the zinc in the solution stirred. In order to reduce the effect of agitation due to the gas itself, the rate of flow was made considerably less than that used in the other series.

SERIES V.

I.	II.	III.	IV.	V.
1	1	4.86	3.53	3.65
2	2	...	2.85	2.80
3	3	...	2.15	2.23
4	4	...	1.73	2.01

The results confirm that of experiment 3, in Series IV, and show that agitation has very little influence upon the rate of precipitation.

Influence of Temperature.—To determine the influence of temperature upon the rate of precipitation, portions of the same solution of zinc chloride were treated at 20° and 50°, respectively, for five hours with hydrogen sulphide flowing at the same rate in each case. Column II, in Series VI, gives the temperature, column III the time, and column IV the zinc remaining in solution. The results show that change in temperature within moderate limits has very little influence upon either the rate of precipitation or the point of final equilibrium.

SERIES VI.

I.	II.	III.	IV.
1	20°	5	1.41
2	50°	5	1.49

Cadmium.—A solution of cadmium chloride was made by dissolving the pure metal in hydrochloric acid. It contained 9.47 per cent. of cadmium and the total acid was 11.33 per cent. The solution gave a pure yellow precipitate with hydrogen sulphide which was free from zinc. The only impurity found was a trace of iron. This solution was treated with hydrogen sulphide in the same way as those of zinc. At the ends of the periods chosen portions were filtered and the cadmium remaining in solution was determined as sulphide, with the usual precautions. In the following table column II contains the time in hours, column III the per cents. of free acid, and IV the per cents. of cadmium remaining in solution.

SERIES VII.

I.	II.	III.	IV.
1	2	8.72	4.00
2	3	9.40	2.96
3	4	9.84	2.42
4	5	10.15	1.81
5	7	10.19	1.75
6	8	10.26	1.64

The general trend of the curve of precipitation is the same as that for the precipitation of zinc from a solution of the chloride, as may be seen by a comparison of the above results with those of Series I, though the approximate equilibrium in the case of cad-

mium is reached much sooner. A comparison of the two is of interest from the analytical point of view. Zinc is by no means all precipitated after many hours from a solution containing 3.18 per cent. of free hydrochloric acid, and the precipitation of cadmium is not complete in a solution containing 10.26 per cent. of this acid. The range of the strength of acid within which it might be considered possible to separate the two metals by precipitation with hydrogen sulphide is, therefore, considerably less than 7 per cent., and a consideration of the curves would lead one to doubt whether it is possible to separate them by a single precipitation with any strength of hydrochloric acid.

Cadmium in Sulphuric Acid Solution.—Cadmium sulphate was made by heating pure cadmium nitrate with pure concentrated sulphuric acid until all trace of nitric acid had disappeared. Experiments showed that cadmium could be completely and quickly precipitated at 20° C. from any strength of sulphuric acid solution. Attention was directed, therefore, to its precipitation at higher temperatures, and for this purpose 85° was the point chosen as convenient. A solution containing about 15 per cent. of free acid and 9 per cent. of cadmium sulphate was treated with hydrogen sulphide at the usual rate for three and a half hours. The cadmium remaining in 13 grams of the solution at the end of this time was only 0.0004 gram, while the amount of free acid as shown by titration was 18.66 per cent.

A second solution containing 9 per cent. of cadmium sulphate and 20 per cent. of free acid was treated with hydrogen sulphide for three hours and at 85°. The cadmium remaining in solution was found to be about the same as above, or only a trace, showing that this metal can be practically completely precipitated from a hot solution containing 22.8 per cent. of free sulphuric acid, this being the amount found by direct titration.

By a comparison of these results with those obtained in Series III, zinc sulphate, it will be seen that while the precipitation of zinc had practically ceased when the free sulphuric acid had reached 5.25 per cent., cadmium is totally precipitated at 85° in the presence of 23 per cent. of free acid. In other words the range of possible complete separation of zinc and cadmium when sulphuric acid is used is at least 17 per cent., or three times what it is when hydrochloric acid is used, and with precipitation at common room temperature the range would probably be much greater.

In view of the fact that cadmium sulphide is soluble in dilute boiling sulphuric acid, the common method of separating cadmium and copper being based upon this fact, it was deemed rather surprising that complete precipitation had taken place at such a high temperature and in the presence of such a quantity of free acid. The following experiment makes clear this seeming anomaly : A portion of the solution, in the last experiment with cadmium sulphate, which contained only a trace of cadmium immediately after the stream of hydrogen sulphide was stopped, was left in contact with the precipitated cadmium sulphide at 85° for half an hour. At the end of that time the solution, now almost free from the odor of hydrogen sulphide, had dissolved 1.8 per cent. of its weight of cadmium sulphide. This result in connection with what has preceded seems to show that the complete precipitation of cadmium as sulphide depends chiefly upon the saturation of the solution with hydrogen sulphide, the temperature and strength of the acid being of only secondary importance. Direct experiment showed that when pure washed cadmium sulphide is allowed to remain in contact with cold dilute sulphuric acid (20 per cent. H₂SO₄) for several hours, it is to a very marked degree dissolved.

I wish to take this opportunity to express my sincere thanks to Dr. W. S. Hendrixson, at whose suggestion this work was undertaken and to whose kind advice and aid any success which this little study may have attained is largely due.

IOWA COLLEGE, GRINNELL,
June 10, 1901.

NEW BOOKS.

ATOMS AND ENERGIES. By D. A. MURRAY. New York : A. S. Barnes & Co. 1901. 202 pp. Illus. 12mo.

The author of this book was some time instructor in the Government Shogyo Gakko, Kyoto, Japan, and he is at present pastor of a Church in a Western city. He claims that the "changed conceptions of the nature of fundamental atomic phenomena" presented in this book, must create a "complete revolution in our thinking along many lines of physical research," and for those who accept his visionary lucubrations this claim will certainly be justified.

According to the author, atoms are all identical in substance

and differ only in size and shape ; he defines an atom as "an Impenetrable Expanse of the ability to Modify and be Moved by Energy." He dwells at length upon the shapes of atoms, for "the one element of Shape in the atom is capable of determining all the varieties of result found in combinations." Thus iron and gold are identical in essence, but their diverse qualities are determined by diversity in shape and size of their atoms. The book contains several illustrations showing the shape of atoms, and they resemble the building blocks used by children and the diagrams of dressmakers. Notwithstanding much space is given to the shape of atoms (pages 43 to 58), the fact that they are endowed with weights is generally ignored !

These atoms are influenced by two energies only, one attracting and one repelling, but "Energy" is not a mode of motion, it is a "distinct Entity." "Adhesion, Cohesion and Chemical Affinity in all its myriad forms," are simply different "operations of Gravitation," and the "key to the solution is to be found in the infinite factor which comes into operation when the atoms are in actual contact with each other." The different kinds of contact are thus explained : "When not in contact we have the Gaseous state ; when but a single point of contact, the Liquid state ; when so many points of contact that there is rigidity, the Solid state ; when face to face contact, Chemical Combinations."

The author demonstrates to his satisfaction that the interstellar Ether is identical with Energy ; he concludes that "the Ether is simply Energy as an Entity."

It is difficult in reviewing a book of this character to avoid doing the author injustice, but we have endeavored to prevent this by citing almost exclusively his own words. The work is endorsed (in an Introduction) by a gentleman who has been successful as an archaeologist and anthropologist, especially in exploring Mexico, but his pursuits have not especially qualified him for judging a treatise on physical science. He says, however, that the work "will stimulate thought."

HENRY CARRINGTON BOLTON.

QUANTITATIVE CHEMICAL ANALYSIS, ADAPTED FOR USE IN THE LABORATORIES OF COLLEGES AND SCHOOLS. By FRANK CLOWES, D.Sc. (LOND.) AND J. BERNARD COLEMAN, A.R.C.Sc. (DUBLIN). Fifth edition. Philadelphia : P. Blakiston's Son & Co. 1900. xxiv + 592 pp. Price, \$3.50.

This is a standard laboratory guide in many of the English

colleges and has also received favor on this side the water. The subject-matter is arranged under sixteen sections. The first three of these describe chemical apparatus, careful chemical manipulation, the determination of specific gravity, boiling-point and melting-point, and the preparation of pure substances. Section IV is arranged so as to be progressive in point of difficulty and includes directions for the gravimetric determination of the more important bases and acids. Volumetric analysis is taken up in Sections V-VIII, beginning with the calibration of burettes, flasks, etc. This could be considerably improved by calling attention more prominently to the necessity of reducing the weight of water to "in vacuo," and giving the correction to be applied for the contraction and expansion of glass. The preparation of, and use of normal solutions are fully explained by practical examples. Section IX is devoted to metallurgical analysis and is the most faulty part of the book. This is probably due to the inferiority of the English to the American methods of metallurgical analysis. For example in this book, zinc is determined in its ore volumetrically by the use of sodium sulphide solution, and silicon in pig iron by evaporation to dryness with nitric acid, etc. The fire assay for lead, silver, and gold, is condensed "past all understanding" into five pages. Sections X and XI are very much better and cover water, food, and soap analysis and the valuation of tanning materials. The methods given for the latter purpose are excellent. Organic analysis and the determination of molecular weights are taken up in Section XII, and the concluding sections treat of simple gas analysis. A collection of tables and miscellaneous matter is appended. The book is well printed and freely illustrated. The methods all through are fully explained and the calculations involved in the analyses are made clear by examples. The entire absence of any references to the periodical literature of the profession and the failure to give credit for the methods, except in rare instances, do not add to the value of the book. Even students should be taught to avail themselves of this wealth of information and experienced chemists usually wish to know sufficient of the history of their methods to enable them to consult the original description and subsequent modifications.

RICHARD K. MEADE.

THE MANUFACTURE OF LAKE PIGMENTS FROM ARTIFICIAL COLOURS. By FRANCIS H. JENNISON, F.I.C., F.C.S. London : Scott, Greenwood & Co.; New York : D. Van Nostrand Co. 1900. iii + 136 pp. 16 plates. Price, \$3.00.

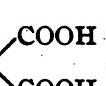
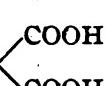
Mr. Jennison has written an interesting and useful book on an important industry whose literature heretofore has consisted of a few scattered chapters or an occasional paper. In the introduction, the author points out the necessity of an intelligent comprehension of the chemistry, constitution and properties of the colors and the subject is treated consistently from this standpoint. This systematic discussion of the industry furnishes a safer guide for the color-maker than empiricism. The few formulas given are types. In the author's words, "It is by far the best plan for each color-maker to carefully examine the color and devise the most rational way to produce the best results, for what works well in one man's hands in a certain place does not, work well with another man in another place."

Three chapters, I, II, and VII, are given to a consideration of the artificial color molecule, beginning with the general principles of synthetic chemistry ; then a description of the most important classes of the colors with examples ; finally, the auxochromes, salt-forming groups, absorption and the function of tannic acid and tartar emetic are considered.

"The Nature and Manipulation of Artificial Colors" is the caption of a chapter on the forms of colors as they appear in the trade with certain recommendations of particular wares of various makers.

A chapter each is given to the description of lake-forming bodies for acid and for basic colors, lake bases, red lakes, other lakes, the insoluble azo colors as pigments, the general properties of lakes, washing, filtering and finishing, matching and testing.

It is an attractive volume embellished with sixteen plates bearing slips of paper coated with lake pigments. These should have been securely gummed, for being secured at only one end they are easily disarranged. Misprints are rather numerous and some astonishing errors are noted : as, "normal hexane, CH₃CH₂CH₂-

CH₃CH₃, isohexane, CH₃CH₂CH₂  , page 5 ; "cinnamic acid, C₆H₅Cl₂  COOH , phenylacrylic acid, C₆Cl₄  COOH" , page

12, and others. "Palmatic" acid, pages 76 and 54, seems to have displaced palmitic.

C. W. PARMELEE.

GLUE AND GLUE TESTING. BY SAMUEL RIDAL, D.Sc. London : Scott, Greenwood & Co.; New York : D. Van Nostrand Co. 1900. viii + 144 pp. Price, \$4.00.

The author aims to give the more important facts connected with the manufacture of glue. In Chapter I the constitution and properties of glue and allied substances are dealt with. This is a topic which most books on this subject do not go into to any great extent. The relations between glue and gelatine are discussed pretty thoroughly, and a table of gelatine-producing substances is copied from Allen. The next chapter considers the manufacture of glue from the raw materials. Starting with the stock it is carried through the liming, washing, cooking, and clarifying process. The need of careful liming and a good supply of water for washing purposes are both emphasized. The use of antiseptics for prevention of putrefaction is mentioned briefly. A few different kinds of kettles, boilers, and evaporators are described and illustrated. Chapter III, in a few pages, states the various ways in which glue is used and the qualities necessary for the different grades. The next thirty pages have to do with gelatine, giving its properties, tests, etc., and describing different forms and the various uses to which they are put.

The chapter on glue testing is somewhat of a disappointment. The title of the book leads one to expect considerably more than is contained in the twenty odd pages given to it. The final pages on "commercial aspects" review the glue trade in general and deprecate the "antiquated policy of exclusiveness," claiming that the custom of keeping "trade secrets" entirely in the dark retards improvement, and works to the disadvantage of the business.

The book on the whole, while covering the ground pretty thoroughly, contains very few original ideas. Liberal quotations are made from similar works.

W. B. BROWN.

SELECT METHODS IN FOOD ANALYSIS. BY HENRY LEFFMANN, A.M., M.D., AND WILLIAM BEAM, A.M., M.D. Philadelphia : P. Blakiston's Son & Co. 1901. 383 pp. Price, \$2.50.

This is one of the most concise and up-to-date books on the subject of food analysis out. While it is intended to be adapted to the needs of advanced students of chemistry as well as the

practising analyst, yet there is nothing of the ordinary text-book style about it. To a large extent the book is a summary of methods and data scattered through the bulletins of the United States Agricultural Department, and of the A. O. A. C., the most of which are now out of print. The authors have also drawn largely upon the works of Allen and Mitchell, and the *Analyst* for considerable of the material. It is divided into two main sections, analytic methods and applied analysis.

The first section on analytic methods describes both physical and chemical operations, such as determination of melting-point, specific gravity, and methods for extraction, distillation, etc., and illustrates some of the newer pieces of apparatus for the same. In describing methods of determining melting-points no mention is made of the acoustical method which is considered very dependable by many chemists. Under nitrogen determinations the Gunning method is mentioned as the most satisfactory, and nothing is said of the straight Kjeldahl method which, for some purposes, is preferable.

Several pages are devoted to the study and identification of starches and flours, giving tables summarizing the characteristics and microscopical appearances of the different starches. In this connection are several plates in the appendix of starch granules reproduced from a government bulletin, the reproduction of which by the way is poor. The examination of food fats and oils, is discussed at some length but is incomplete in some ways.

The matter in the sections on milk, butter, and cheese, is similar to the contents of the author's excellent little book on "Milk and Milk Products," but it has been revised and made more practical, and now contains all the information necessary for the analysis of milk products.

The last 100 pages take up such subjects as the examination of tea, coffee, spices, extracts, alcoholic beverages and flesh foods.

There is an appendix containing a few tables, followed by plates of starch granules and leaves all reproduced from Bulletin 13, U. S. Department of Agriculture. The book is bound the same as the latest edition of Allen's "Commercial Organic Analysis."

W. B. BROWN.

PURE AIR, OZONE AND WATER. A practical treatise of their utilization and value in oil, grease, soap, paint, glue, and other industries. By W. B. COWELL. London: Scott, Greenwood & Co.; New York: D. Van Nostrand Co. 1900. vii + 85 pp. Price, \$2.00.

This is a small volume of 85 pages, and has to do with the applications of pure air, ozone, and water in industrial works. The author describes briefly the various uses to which air, ozone, and water may be put in technical works to aid in manufacturing processes, purifications, etc.

It is a practical book from the ordinary manufacturer's standpoint and is almost free from technicalities, but for the scientific man who is at all familiar with the methods used and principles involved in technical industries there is little new. One chapter takes up the purification of water and its uses for boiler purposes, all of which may be found in a dozen or more books.

There is an appendix which contains considerable valuable information, giving tables of temperatures, solubilities, properties of steam, and rules for measurements.

The book is well printed in large type on good paper.

W. B. BROWN.

EXPERIMENTS ARRANGED FOR STUDENTS IN GENERAL CHEMISTRY. By EDGAR F. SMITH AND HARRY F. KELLER. Fourth edition, enlarged. 88 pp., interleaved. Philadelphia: P. Blakiston's Son & Co. 1900. Price, 60 cents.

The earlier editions of this book are already familiar to many teachers, and have been characterized by the good judgment shown in the selection of experiments and the clearness of the directions given to the student. The suggestive questions on the experiments and the problems in chemical arithmetic are also to be commended.

This edition brings the book more into line with the newer ideas in teaching chemistry, by the addition of quite a number of new experiments, but this is not done at the expense of those experiments which illustrate descriptive chemistry. Judging by recent books, there seems to be a tendency to-day to neglect all of chemistry which cannot be treated quantitatively. The authors have preserved a good balance in this respect, giving a fair number of quantitative experiments, such as the determinations of the weight of a liter of chlorine, oxygen, steam, nitrogen, and ammonia; the volumetric composition of water, and of hydrochloric

acid gas; the equivalent weight of zinc, and of tin; the volumetric analysis of caustic soda, and of iron; and the specific heat of tin.

In this improved edition, the book is one of the best of the many laboratory manuals in print. JAS. LEWIS HOWE.

IRON CORROSION; ANTI-FOULING AND ANTI-CORROSIVE PAINTS. BY LOUIS EDGAR ANDÉS. London: Scott, Greenwood & Co. New York: D. Van Nostrand Co. 1900. viii + 275 pp. Price, \$4.00.

The extensive and important use of steel as structural material, which practically began about ten years ago, owing to the improvements in metallurgy which lowered the price of steel until its use became economical, has made the subject of this book one of great importance. Cast iron is not very easily corroded; and moreover is used in thick pieces which will stand considerable corrosion; but the opposite is the case with steel. The last preceding book on the subject was issued in 1895, and was of little value; hence much interest attaches to a new book. Like other books about other things by this author, this treatise contains practically no original matter, but gives the results of some of the more important German papers on the subject. The comparison of different passages will therefore give contradictory views on the same topic; but in such a work this is inevitable, and is nothing against it. The numerous illustrations are of very little value; and the whole treatise, which is a short one (about 80,000 words), reads as though the author were rather short of material to fill the book. The chemical part of the work is of more interest to the general reader than to the analyst, as is proper; but references to chemical literature might have been added with advantage. A rather interesting chapter is given on the composition of patent and proprietary paints, and a few pages of much value on specifications. The book is probably the best one on the subject, to date, but it is fragmentary, does not give recent English or American work on the subject, and leaves one with the impression that there is still room for a more elaborate treatise on the protection of structural metal. A. H. SABIN.

TRAITÉ DE LA FABRICATION DES LIQUEURS ET DE LA DISTILLATION DES ALCOOLS. PAR P. DUPLAIS AINÉ. Septième édition, entièrement refondue par Marcel Arpin et Ernest Portier, en deux tomes. Paris: Gauthier-Villars, Quai des Grands-Augustins, 55. 1900. 1219 pp. Price, 18 francs.

This well-known work of Duplais, of which the earlier edition

was translated and appeared in an American issue, has recently been brought out in a seventh edition, which the present editors say has been thoroughly revised and in part rewritten. This applies, as the preface tells us, particularly to the first volume, that treating of the alcohols, their preparation and technology, while the second volume upon the liqueurs and alcohol containing products has not been so notably changed.

Duplais' work, as indicated by the full title given above, is mainly concerned with the manufacture of alcoholic products and this part of the work (Vol. II) will no doubt be considered as still entitled to the character long possessed by it, of being a standard authority upon the making of liqueurs and similar products.

The whole art of compounding these alcohol-containing products is explained and illustrated, the preparation of aromatic distilled waters, of tinctures and infusions, and of the nature of the volatile oils which are used and the means of recognizing their purity are covered, as is also the preparation of the sugars, syrups, and colors used. The manufacture of conserved fruits and factitious wines is also fully described and a chapter is devoted to the manufacture of carbonated waters and effervescing alcoholic liquids of artificial origin.

An alphabetically arranged account of the principal plants and drugs employed by the liqueur manufacturer is given, which puts together in convenient form quite an amount of information useful to the manufacturer.

Vol. I, devoted to the alcohols and covering the questions of fermentation and treatment of the products therefrom, is not of the same relative value. In this field there are a number of other works, both special and of general character that are more satisfactory. Thus, while this new edition of Duplais' notes Hansen's work on pure yeast cultures, it does not discuss the broader question of the part which soluble ferments play in the distilling industries. Works like "Les enzymes et leur applications" by J. Effront, published in 1898, "Soluble Ferments and Fermentation," by J. Reynolds Green, published in 1899, and the German edition of Effront's work by M. Bücheler, published in 1900, are much more valuable for this purpose. Fuller discussion of the methods of alcohol rectification and purification are also found in Barbet's "Manuel des Fabricants d' Alcools," Paris, 1894.

In its present form, Duplais' work will, however, be of value to

those interested in the liqueur manufacture and continue its reputation as a standard authority. SAMUEL P. SADTLER.

A MANUAL OF LABORATORY PHYSICS. By H. M. TORY AND F. H. PITCHER. New York : John Wiley & Sons. 1901. 8vo. ix + 288 pp. Price, \$2.00.

This little manual embodies in book form the directions for the performance of the various experiments given in the course in elementary physics at McGill University, Montreal.

The arrangement and presentation of the subject-matter is original and somewhat novel, and is, as stated in the preface, "the outgrowth of experience in teaching large classes with a limited number of instructors."

Explanations and directions for 84 experiments are given. These are distributed as follows : Sound, 10 ; Light, 21 ; Heat, 9 ; Magnetism, 9 ; Electricity, 35.

The directions for each experiment are divided into a number of sections: 1. "References" for collateral reading; 2. "Apparatus Required;" 3. "Theory of Experiment;" 4. "Practical Directions;" 5. "Example" illustrating the data and results to be obtained ; and lastly there is given a blank which is to be filled out by the student after the completion of the experimental work.

The directions are brief and terse, yet quite to the point. It is evident that there has been a studied effort on the part of the authors to give just what is absolutely essential, and to do this in as few words as possible.

As in all manuals of a similar nature there is the unavoidable local flavor as to apparatus and methods. It must be said, however, that the authors have apparently succeeded admirably in reducing this to a minimum and have so presented their subject that the book can be used as a manual in any properly equipped institution.

Viewed from the standpoint of the physicist, the experiments are doubtless well selected and described ; but from the chemist's point of view, it is to be regretted that the authors have omitted experiments which, it would seem, should be given to every student intending to follow up the natural sciences, as, for example, experiments dealing with polarized light, etc.

The manual is up to the usual excellence of the publishers, the paper being heavy, of good quality, and the impression neat and clear.

E. M. C.

PUBLIC WATER SUPPLIES, REQUIREMENTS, RESOURCES, AND THE CONSTRUCTION OF WORKS: BY F. E. TURNEAURE, C.E., AND H. L. RUSSELL, PH.D., Professors in the University of Wisconsin. New York: John Wiley and Sons. 1901. xiv + 746 pp. Price, \$5.00

The preface states that the volume is prepared with particular reference to the needs of teachers and students of technical schools; and that the specialist need look for little that is new, although it is hoped that the form in which a large amount of widely scattered information has been presented will prove a convenience to him.

An examination of the book shows it to be by far the most complete treatment of the subject which has yet appeared, resembling in many respects the elaborate German handbooks rather than the earlier American text-books on the subject. Following German precedent is particularly commendable in the very complete and up-to-date bibliography at the end of each chapter.

The study of public water supplies involves not only civil engineering and biology, but chemistry, mechanical engineering, and in fact nearly all the arts and sciences. The treatment of the subject by the authors has been facilitated because they represent respectively the two most important divisions of the subject, namely, civil engineering and biology; and as a result both the engineering and the hygienic sides of the subject have received ample consideration at every point, while the chapter on pumping machinery, which gives a comprehensive idea of the elementary principles involved, was prepared by a specialist, Mr. D. W. Mead, of Chicago.

Without attempting to take up the endless details which constitute so large a part of water supply engineering, but which, for the most part, can only be learned by actual practice, the authors have stated briefly the principles of the art, and have usually given at least an idea of the basis upon which each rests. The completeness with which even the most recent investigations and publications have been noted and used in the preparation of the work is an evidence both of the industry and thoroughness of the authors, and of the rapidity with which the publishers have put the volume through the press.

A work of this character is necessarily based largely upon previously published records, and in using such records the authors

have uniformly given credit to the original authors, which is at once simple justice to them, and a convenience to the student who wishes to know the sources of the various data given. In a few cases translations or abstracts have been referred to as if they were original articles; but this slight failing only emphasizes the general excellence of the work. The book is well printed and freely illustrated throughout.

ALLEN HAZEN.

THE MINERAL INDUSTRY : ITS STATISTICS, TECHNOLOGY AND TRADE IN THE UNITED STATES AND OTHER COUNTRIES, TO THE END OF 1900.
FOUNDED AND EDITED BY RICHARD P. ROTHWELL AND COMPLETED BY JOSEPH STRUTHERS, PH.D. Vol. IX. New York and London: The Scientific Publishing Company. xxx+918 pp. Price, \$5.00.

This is the ninth annual volume of a series begun in 1892 and edited by Mr. Rothwell, who died on April 17, 1901. The series has contained information of great interest and value to the metallurgist. The present volume seems to maintain the high standard of excellence reached by those preceding it. Among the special articles contained in this volume, aside from the progress reports, are those on "The Emery Deposits of West Chester County, N. Y.," by E. C. Eckel; "Production of Bromine in Michigan," by A. C. Lane; "Calcium Carbide and Acetylene," by L. K. Böhm; "Clay and its Manufacture into Brick and Tile," by H. Ries; "The Manufacture of Water-gas, with Special Reference to European Conditions," by G. Lunge; "The Utilization of Blast-furnace Gases for the Direct Production of Motive Power," by G. Lgune; "The Utilization of Lignite in Germany," by P. Krusch; "The Raritan Copper Works," by L. Addicks; "Diamondiferous Deposits in the United States," by W. H. Hobbs; "A Report on Iron and Steel Metallurgy at the Paris Exhibition," by H. M. Howe; "Alloys of Iron," by H. Souther; "The Manufacture of White Lead," by P. C. McIlhaney; "A Review of the Tin Industry of the Malay Peninsula," by F. Owen.

During the year the industry increased in value \$147,393,946, reaching the sum of \$1,365,608,583. The total production of iron ore in the United States was 25,917,393 long tons, of pig iron 13,789,242 long tons, and of steel 10,218,572 long tons. This represents about one-third of the world's production. The coal product in 1900 was 52,131,212 metric tons antracite and 191,256,216 metric tons bituminous, a total of 243,414,163 (including cannel coal), and an increase of 14,696,584 tons over the total for 1899. The total excess of exports over imports was nearly 6,000,000 tons, an increase of about 1,750,000 tons over 1899. Our coal forms now about one-third of the world's production.

Our copper product in 1900 was 600,832,505 lbs., an increase

of 20,000,000 pounds. This is more than half the world's product. Of lead we produced 411,568 short tons, and of zinc 123,231 short tons.

Nearly all our potassium chlorate, about 6,000,000 pounds per annum, is now manufactured at home by electrolytic processes. We are the largest producers of salt (in 1900 20,738,729 barrels of 280 pounds), of gold (3,781,310 ounces), of silver (59,561,797 ounces), of phosphate rock (1,663,476 net tons), and second only to Russia in petroleum output.

This year has witnessed a great increase in the cement industry (7,991,639 barrels of Portland cement). Of the Portland cement three-quarters is produced in the states of Pennsylvania and New Jersey. The opinion is expressed that the cheapest producing territory is likely to be found in the Lehigh Valley where the industry has already had enormous development.

It is quite impossible in the space available to give an adequate idea of the vast amount of data of all sorts contained in this magnificent report of progress.

E. H.

AN ELEMENTARY TREATISE ON QUALITATIVE CHEMICAL ANALYSIS.

By J. F. SELLERS, A.M., Professor of Chemistry, Mercer University, Georgia. Boston: Ginn & Co. 1900. ix + 160 pp.

Within the compass of 137 pages, the author seeks to present "a course both practical and progressive * * * selected from the most recent and approved methods * * * free from the mechanical schemes in qualitative analysis * * * and conformable to the modern dissociation theory of solutions and giving * * * more than ordinary emphasis to the spectroscope."

The reviewer has read the various chapters with great interest. The impression made is that almost too much has been attempted, and that comparatively few of the students, who may pursue the course from beginning to end, as it is presented, would really become "practical analysts" or be thoroughly prepared "for advanced university work." From the reviewer's experience to attain to either of these states, would require a decidedly more exhaustive and thorough drill than seems to be intended by the author. It is hardly likely, for example, that a beginner, in carrying out the instructions for the decomposition of an insoluble silicate by the J. Lawrence Smith method, as described on page 133, would meet with much success, because of a lack of detailed directions as to how he should proceed. Other and similar instances of incomplete descriptions of analytical methods exist but they need not be pointed out, as the teacher and student will of course discover them for themselves. It only remains to say that the book is well written and will doubtless be acceptable to those who do not lay great stress upon drill in analysis.

EDGAR F. SMITH.

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[AUGUST, 1901.]

No. 8.

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AMERICAN CHEMICAL SOCIETY.

RESEARCHES ON NITROCELLULOSE.

BY G. LUNGE.

Received June 26, 1901:

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- A. Estimations of nitrogen.
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- D. Examination under the polarization microscope.
- E. Behavior of nitrocellulose towards iodine.
- F. Estimation of unchanged cellulose in nitrocelluloses.

III. Methods for obtaining the various nitrocelluloses. Former views on the formulas of nitrocelluloses.

- A. On the highest stage of nitration obtainable from cellulose.
- B. Various conditions to be observed in the nitrating process.
- C. Influence of water on the nitrating process.
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- I. Behavior of different commercial grades of cotton in nitration, especially for the manufacture of collodion cotton.

INTRODUCTION.

The work reported in the following pages has been carried

out during the years 1897 to 1900, the first part with the cooperation of Dr. Weintraub, the second with that of Dr. Bebie. In the description which I shall give of these researches, I shall not adhere to their chronological sequence, but group them in their logical order, the later researches being sometimes only confirmatory or supplementary to some carried out at a previous stage, and sometimes modifying the conclusions previously arrived at. This present report consequently affords a clearer picture of the ultimate results of our work than the separate German publications, and embodies also a few facts that later came to my knowledge.

The object of this investigation was to study the conditions under which nitrocelluloses of various composition and various properties can be regularly and with certainty prepared, and to establish both the composition and the properties of the products obtained under varying circumstances with greater accuracy than had been done up to that time, as witnessed by the considerable discrepancies among the statements of different authors.

My ultimate object was to try whether the technology of nitrocelluloses could not be advanced somewhat more beyond the classical researches of Sir Frederick Abel than had been done by the various publications of subsequent authors, meritorious as these are, especially as their opinions differ in important matters, and sundry points of great moment had not been at all elucidated.

It is hardly necessary to say that I cannot pretend to approach the unique work of Abel, if for no other reason, because the work of my cooperators and myself was confined to the resources of a well equipped laboratory, whereas he had an opportunity of testing his results on a large scale, and thereby, as all the world knows, laid the foundation of the present industry of guncotton. Nor is it necessary to say that very possibly similar work to that which we have carried out at Zurich may have been done in the secrecy of factory laboratories, and the result applied to practice. Of this secret work, if such has been done, I have absolutely no knowledge, nor is it the property of the industrial world in general, and the science of technology is thereby no more benefited than are the interests of other manufacturers than those for whom it has been specially undertaken. I make this remark in view of the

¹ Compare the former with: *Ztschr. angew. Chem.*, 1899, pp. 441 and 467; the latter is in course of publication in the same *Zeitschrift*.

possibility that after my publication somebody may say that this or that part of my results has been already known to him. Such *private* information should not debar others from pursuing the path of knowledge in the general interest of science and industry. But I am not aware of any such work having been done privately on the same lines as ours, and I can only deal with what is to be found in literature.

I. GENERAL REMARKS ON THE METHODS EMPLOYED FOR NITRATING CELLULOSE.

The material employed throughout the work (except for the special purpose described in Section III, *I*), was the so-called "chemically pure surgical cotton wool." In order to remove the last traces of fat, it was boiled for some time in a weak solution of sodium carbonate, well washed with water and extracted with alcohol and ether. The percentage of ash found = 0.06 per cent. on the average of several estimations. Immediately before nitration the cotton wool was dried at 100° till the weight was nearly constant, allowed to cool in the desiccator, and at once placed in the nitrating vessel.

The acid mixtures were made from weighed quantities of "chemically pure" sulphuric acid (sp. gr. 1.84) and fuming nitric acid (sp. gr. 1.52). The former as used for the first part of this work showed an analysis of 95.62 per cent. H₂SO₄, the latter 93.76 per cent. HNO₃, and from 1 to 2 per cent. lower oxides which were removed in the ordinary way. For the second part of the work, where more particular attention was paid to the exact percentage of water present, the mixture was always analyzed when complete, and its exact composition is stated in the respective sections.

For carrying out the nitrations the apparatus shown in Fig. 1 was employed. A stout cylindrical jar, *A*, was closed by means of a tightly ground-in glass cover, *B*, provided in the center with a drop-funnel, *C*, and on one side with a tube, *D*, bent at a right angle and closed by a glass tap, both of them sealed to the glass cover *B*. The latter was further perforated for admitting a thermometer, *E*, which was fixed perfectly tight by means of asbestos and sodium silicate solution.

The cellulose was placed in the jar, the cover put on, and the acid mixture poured into the drop-funnel. The lateral tube was

connected with a good Bunsen pump, and nearly all the air was thus removed from the jar and the cotton wool. Now the connection with the Bunsen pump was shut off, and the acid slowly run in from the drop-funnel. For nitrating at higher than the ordinary temperatures the acid mixture was heated a little above the desired temperature, placed in the drop-funnel, and after cooling down to the proper point, run on the cotton. The temperature within the vessel was regulated by placing it in a large water-bath. Sometimes, in the case of operations taking a long time and going on over night where temperature observations were impossible, the described apparatus was replaced by ordinary wide-mouthed jars with ground-in stoppers.

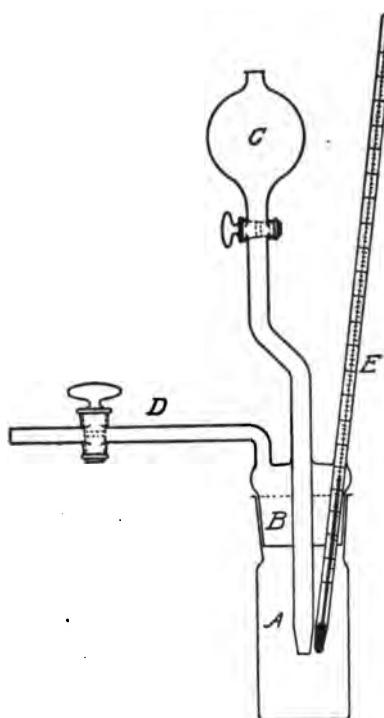


Fig. I.

When the action of the acid had lasted sufficiently long it was separated from the nitrocellulose first by decantation and secondly by the action of the vacuum pump, employing a porcelain funnel with porcelain sieve. The mass was placed in cold water and quickly moved about in order to avoid any considerable rise of temperature. The washing was performed first with cold, then with hot, water, and before each renewal of the water the nitrocellulose was again freed from liquid by means of the vacuum funnel.

The washing requires various lengths of time, according to the physical structure of the nitrocelluloses,—usually two or three days. Later on we shall describe the washing processes employed in special cases.

The mode of operation just described could be employed only in those cases where the nitrocellulose retained a structure similar

to that of the cotton fiber. When employing acid mixtures containing a large excess of sulphuric acid, this structure is destroyed; this product consists of short fibers, suspended in the liquid. In this case, after the nitration has been completed, the whole was poured into an excess of ice-water and then filtered through a porcelain funnel whose sieve-plate was covered with linen or filter-paper. The nitrocellulose was then washed by decantation in a large Erlenmeyer flask.

After washing, the nitrocellulose was dried either in a vacuum-desiccator protected against light or else in a special apparatus shown in Figs. 2 and 3, by means of a current of dry air at a temperature of 40° in the earlier, or from 30° to 32° in the later experiments, (the latter temperature having been found to be sufficiently high). For this purpose the product was placed in a cylindrical glass vessel, *A*, contracted at the bottom into a tube *a*, bent at a right angle. Just above the concentration a porcelain sieve, *b*, is placed, on which the nitrocellulose rests. The top is closed by a ground-in glass cover, *c*, with a lateral tube, *d*, and a hole in the center for a thermometer reaching *e* down to the substance. Usually two sets of apparatus were employed at the same time by connecting the inlets *a* with a T-tube supplied with air dried by calcium chloride and sulphuric acid. Both vessels, *A*, were placed in an asbestos box, *B*, whose bottom was heated by a very small gas-jet. The four sides of the box were made from a piece of asbestos cardboard, cut half through lengthwise and bent round to form a square tube, the last edge being formed by

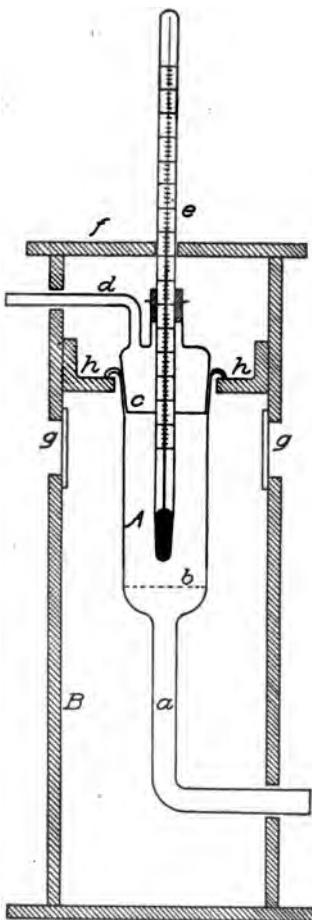


Fig. 2.

means of iron wire clamps and strengthening all the joints with asbestos paper soaked in water-glass solution. The cover *f*, also made of asbestos, is movable and is perforated for the passage of the thermometer *e*. Tube *A* is suspended by means of small glass lugs on the edges *h h*. One of the sides of the box *B* has two openings near the bottom for the air-supply pipes *a* and another side has openings for the air-escape pipes *d* near the top; half way up, at the level of the nitrocellulose, there are small glass windows *g g*, opposite each other which allow of observing the process. The box is placed on an asbestos plate, and by means of a small gas-jet the temperature can be kept constant to 0.5° or at most 1° during several hours, while air, which has passed through calcium chloride and sulphuric acid, is passed in at *a* and passes out at *d*.

This asbestos oven, which it takes about an hour to construct, has done us excellent service. It admits of drying the nitrocellulose in a current of dry air at the desired temperature which is attained within the asbestos box in contact with the glass vessel. On the large scale, of course, the air would be previously heated to the requisite point; but this is very difficult to attain with any degree of accuracy in a laboratory apparatus and is quite unnecessary, when using the arrangement described.

The exit-tube *d* is connected with a flask containing concentrated sulphuric acid, in order to retain any nitrous vapors evolved from the nitrocellulose during the drying process.

This apparatus effects a very great saving of time as compared with drying in the desiccator. Nitrocellulose carefully freed from water by pressing requires seven or eight days' drying in the desiccator, but only twelve to fifteen hours in the asbestos oven, to attain constancy of weight. Check tests made of the same sample of nitrocellulose with both modes of drying never showed any appreciable difference in the nitrogen percentage. A very slight loss of nitrous vapors, however, does take place, although unappreciable by the most careful analysis of the product, for the sulphuric acid through which the exit air was passed usually destroyed two or three drops of decinormal permanganate. Therefore in more important cases the slower, but absolutely certain, method of drying in the desiccator was preferred.

II. ANALYTICAL METHODS.

A. The Estimations of Nitrogen were always performed in my well-known gas volumeter (five-part nitrometer). The nitro-cellulose was dissolved in concentrated sulphuric acid in the funnel of the agitating-vessel, provided with a rubber stopper and swan-neck tube; only the short fiber products which cannot easily be put into the funnel without loss by dusting were dissolved in a stoppered weighing-bottle. Usually the solution was effected in from half an hour to an hour; exceptionally the close quality of a product caused it to be very slowly penetrated by the acid, in which case the operation lasts up to twenty-four hours. The results are exceedingly accurate; the difference among various estimations is rarely more than 0.1 to 0.2 cc. NO per 1 gram, which means about 0.01 per cent. nitrogen.¹

Williams² asserts that, if the nitrometer funnel is rinsed first with concentrated and afterwards with slightly diluted acid, the results are 0.2 per cent. higher than when using concentrated acid alone, owing to the rise of temperature produced in the former case, which is necessary for completing the decomposition. This assertion is not correct, as was shown by very careful estimations, in which the same sample was tested (1) by rinsing with concentrated acid only and (2) by employing dilute acid at the end:

	Nitrogen. Per cent.	Nitrogen. Per cent.
(1)	13.30	13.28
(2)	13.27	13.29

We tested also Chenel's method,³ which is a modification of Kjeldahl's method. The results were satisfactory, but this method is far more troublesome and lengthy than the nitrometer method, so there is absolutely no reason for preferring it to the latter which is at least equally accurate.

The English and German way of stating the results is to quote the percentage of nitrogen; in France the results are stated as the number of cubic centimeters NO (reduced to 0° C. and 760 mm. pressure) evolved by 1 gram of the substance.

15.95 cc. NO = 1 per cent. N;

1 cc. NO = 0.0627 per cent. N.

¹ The difference between the atomic weights ordinarily used in calculations (O = 16, N = 14, C = 12, H = 1), and the exact atomic weights (O = 16, N = 14.04, C = 12, H = 1.008) amounts to more than the above discrepancies.

² *Moniteur Scientifique*, 1899, p. 920.

³ *Mém. des poudres et salpêtres*, 8, 45.

To facilitate comparisons I append the following table, calculated with the exact atomic weights accepted by the German Chemical Society.

TABLE I.

Degrees of nitration.	Formula.	Nitrogen. Per cent.	NO per 1 gram. cc.
Dodecanitrocellulose (=old trinitrocellulose)	C ₂₄ H ₂₀ O ₂₀ (NO ₂) ₁₂	14.16	225.53
Endecanitrocellulose	C ₂₄ H ₂₀ O ₂₀ (NO ₂) ₁₁	13.50	215.32
Decanitrocellulose	C ₂₄ H ₂₀ O ₂₀ (NO ₂) ₁₀	12.78	203.87
Enneanitrocellulose	C ₂₄ H ₂₀ O ₂₀ (NO ₂) ₉	11.98	191.08
Octonitrocellulose (=old dinitrocellulose)	C ₂₄ H ₂₀ O ₂₀ (NO ₂) ₈	11.13	177.52
Heptanitrocellulose	C ₂₄ H ₂₀ O ₂₀ (NO ₂) ₇	10.19	162.53
Hexanitrocellulose	C ₂₄ H ₂₀ O ₂₀ (NO ₂) ₆	9.17	146.26
Pantanitrocellulose	C ₂₄ H ₂₀ O ₂₀ (NO ₂) ₅	8.04	128.24
Tetranitrocellulose (=old mononitrocellulose)	C ₂₄ H ₂₀ O ₂₀ (NO ₂) ₄	6.77	108.01

In the original papers the results are generally stated in cubic centimeters NO, but as this is less familiar to Anglo-American readers, I have translated them all into nitrogen percentages.

In the first series of experiments (of which there were several hundreds performed) the *yields* were regularly determined; later on this was only occasionally done, as this repetition seemed unnecessary.

B. Wherever the solubility in ether-alcohol had to be determined, one of the two following methods was followed: Where only a few per cent. of soluble matter is present, this can be extracted by ether-alcohol, and the insoluble residue dried and weighed. This process does not answer where there is much soluble matter present, because in this case the solution is too viscous and too difficult to filter and the residue too gelatinous for proper washing. In these cases the English method was employed: Treating the substance in a stoppered cylinder with a certain quantity of ether-alcohol, allowing to settle, withdrawing a portion of the clear supernatant liquid by means of a pipette, evaporating and drying at 50° till the weight is constant. By this process the soluble nitrocellulose is converted into a tough compact mass which it is very difficult to entirely free from the solvent; hence the results are too high; in the case of perfectly soluble nitrocellulose usually 102 or 103 per cent. was found. Better results were obtained by precipitating the nitrocellulose from the solu-

tion in a flocculent form by careful addition of water before evaporation, with constant stirring, until a permanent turbidity was produced.

The solvent usually employed was a mixture of three parts ether (sp. gr. 0.72) and one part alcohol (sp. gr. 0.81), but we shall see in Section III, G, that the same results are obtained by many other proportions of these ingredients.

C. The Analysis of the Acid Mixtures was performed according to the methods described in my "Taschenbuch für Soda-fabrikation" 3rd edition, p. 249. (This is a somewhat enlarged and improved form of the methods given in Lunge and Hurter's "Alkalimaker's Handbook," 2nd edition, p. 155.)

D. Examination of the Nitrated Celluloses under the Polarization microscope.—The statements found in literature on the behavior of nitrocelluloses in polarized light show great discrepancies. In Muspratt-Stohmann's Chemistry (1869) it is stated that gun-cotton, when observed under the microscope in polarized light, exhibits no, or almost no, color, whereas cotton fiber shows bright and beautifully variegated colors. Morton Liebschütz (*Moniteur Scientifique*, 1891, p. 119) says that the compound which he calls hexanitrocellulose (our dodecanitrocellulose) can be recognized by its greater brilliancy and slate-gray color; penta- (our deca-) nitrocellulose by its blue color; tetra- (our octo-) nitrocellulose by its yellow color. Guttmann¹ says: "If examined under the microscope with polarized light, ordinary cotton is colorless while guncotton exhibits colors." This is a clerical error, as stated by Guttmann in his contribution to my "Chemisch-technische Untersuchungsmethoden," Vol. II, p. 477. Chardonnet² makes the following statement: Up to 6.9 per cent. nitrogen the nitration can be recognized only by a few large, shrunk-up fibers; from 6.9 to 9.1 per cent. nitrogen there are more such fibers, and a few rainbow-colored ones; from 9.15 per cent. on the fibers turn more evenly gray; from 10.0 to 11.28 per cent. they turn straw-colored to orange; above 11.28 per cent. nitrogen the fibers appear first colorless, afterwards purple, dark blue, and light blue, the last color becoming prevalent as the nitrogen increases. When all fibers are equally light blue, the action is finished.

The continued observation of our products, along with their

¹ "Manufacture of Explosives," Vol. II, p. 59.

² According to Wyss-Naef: *Ztschr. angew. Chem.*, 1899, p. 31.

careful analysis, has led to the following conclusions which I believe to be quite correct. The most highly nitrated products show in polarized light a blue color. These products, whose nitrogen percentage varies between 13.9 and 13.0, cannot be distinguished from each other by polarization. As the nitrogen percentage rises, the blue color becomes less intense, but decidedly never turns slate-gray or colorless. Certainly some gray fibers can be observed here and there, but not in proportion to the increase of nitrogen. On the contrary, the highest degrees of nitration (13.9 per cent. nitrogen) appeared almost purely blue, and in products of only 13.0 most fibers were gray, although there was always a mixture of both present, and it was observed that on turning the object table, gray fibers flashed up in a blue light and *vice versa*, that is to say, the blue color appears in a certain position, and the gray color in another.

The purple transition shade mentioned by Chardonnet could not be observed. From 12.4 per cent. downwards most fibers showed a gray luster which, when keeping off the top-light, mostly turns faint yellow, but sometimes remains unchanged. This goes down to 10.66 per cent.; below 10 per cent. nitrogen the structure was always partly destroyed and no certain observations could be made. But when we come to unchanged cellulose, we find this decidedly and strongly flashing up yellow to orange, and here and there with rainbow colors. As the effects of polarization are produced not merely by the chemical composition, but also by the physical structure of the fibers, it is out of the question to make such sharp distinctions as stated by some of the previous observers. All we can say is, we can *with certainty* distinguish firstly, any *unchanged cellulose* by its very strong flashing up in yellow, orange, and variegated (rainbow) colors; secondly, highly nitrated products (from 12.75 per cent. nitrogen upwards) by flashing up not so strongly in blue colors. Further distinctions are *not* possible, even in the case of high degrees of nitration. When working for collodion cotton, where the structure of the fiber is to some extent affected, and there is more unchanged cellulose present, the polarization microscope renders no practical service. In the presence of only 5 per cent. unchanged cellulose a great part of the microscopic field appears yellow, and with 15 per cent. cellulose the phenomena of polarization of the nitrated fibers are entirely obscured. Hence the polarization is a

useful means for qualitatively detecting the presence of small quantities of unchanged cellulose in highly nitrated products, but it fails in the case of collodion cottons.

E. Behavior of Nitrocellulose towards Iodine.—According to Guttmann,¹ Kindt states that when treating nitrated cellulose with a solution of iodine in potassium iodide, and subsequently moistening with dilute sulphuric acid, guncotton becomes yellow, while cotton turns blue. We found when following this direction, that the yellow or brown color does not proceed from any action of iodine upon the nitrated fiber, for it is entirely removed by washing. When treating with iodine solution alone, without sulphuric acid, and subsequently washing with water, the most highly nitrated products (guncotton proper) lost their color; the less strongly nitrated products retained a brown color increasing with the *decrease* of nitration, but not at all with sufficient regularity to base any clear distinction thereon. In all probability, this phenomenon is caused by the formation of oxycellulose, of which several modifications are known to exist.² At any rate, the above-mentioned reagent did not prove of any value.

F. Quantitative Estimation of Unchanged Cellulose in Nitrocelluloses.—During the progress of our work, the necessity frequently arose for quantitatively estimating any admixture of unchanged cellulose in the nitrated products. The methods described up to that time were thoroughly tested, but yielded quite unsatisfactory results. The oldest of these is based on a treatment with a hot concentrated solution of sodium sulphide; this is a very slow process and we never succeeded in obtaining a residue free from nitrogen. Hess and Schwab, and later on Eder, decomposed collodion cotton dissolved in ether-alcohol by an alcoholic solution of potash or soda, and this is also applicable to guncotton when dissolving this in acetone, but it is not easily carried through because the solution of sodium hydroxide in almost anhydrous alcohol takes place with great slowness, while the presence of a little more water militates against the reaction.

The following new process was found to answer the purpose in the case of the mere highly nitrated products. The reagent employed is an alcoholic solution of sodium ethylate (sodium methylate or amylate have the same effect), C_2H_5ONa , prepared

¹ *Loc. cit.*, 2, 59.

² Compare Section III, F.

by dissolving 2 or 3 grams metallic sodium in 100 cc. 95 per cent. alcohol, which takes only a few minutes. The solution is filtered and is mixed with 100 cc. acetone. This reagent has no effect whatever on real cellulose, even after an action of several hours' duration, but nitrocellulose is almost instantaneously decomposed with formation of a reddish brown substance soluble in water, evidently the sodium salt of an organic acid, possibly connected with Will's oxypyruvic acid.¹ The operation is carried out as follows:

150 cc. of the 200 cc. prepared above are placed in a capsule or Erlenmeyer flask along with 5 grams of guncotton. The mixture is heated to 40° or 50° on a water-bath, and now and then shaken up during twenty or thirty minutes; or else it is allowed to stand at the ordinary temperature for a few hours. It is then allowed to settle. The brown-red solution is decanted from the undissolved portion; the latter is first washed with alcohol by decantation, and subsequently with water, whereby the brown substance is dissolved. The residue, consisting of cellulose, is filtered and washed with hot water, last of all with addition of a little hydrochloric acid. For ordinary work, it may be at once dried and weighed; for very exact estimations the water is removed by washing with alcohol, the residue is once more treated with 50 cc. of the reagent left over from the first treatment by keeping at 40° or 50° for fifteen minutes, and the operation is finished as above. The cellulose thus obtained does not yield a trace of gas in the nitrometer and gives only an extremely faint blue reaction with diphenylamine. It shows a very faint yellow color, produced by about 0.1 mg. of the brown substance which can be removed by treating with a solution of 0.1 mg. chloride of lime in 5 cc. very dilute hydrochloric acid; but this last treatment is really unnecessary, as the 0.1 mg. does not appreciably affect the estimation. The results agree to 0.1 or 0.2 per cent., if the weight of unchanged cellulose amounts to about 0.2 gram, which can be attained by employing a convenient weight of guncotton.

Guncotton entirely soluble in acetone contains only traces of cellulose. In the presence of 0.85 per cent. cellulose, the solubility is impaired; some fibers remain floating in the liquid. When 5 or 10 per cent. cellulose is present, a great part of the nitrocellulose does not dissolve in acetone.

¹ Ber. d. chem. Ges., 24, 400.

The described reagent, sodium ethylate, is applicable to the estimation of cellulose in guncotton and collodion cotton, but not in the products with lower nitrogen percentages which have as yet no technical application, but were prepared by us in order to study the various degrees of nitration (Section III, C). In the case of these products, which always contain much unchanged cotton fiber, the sodium ethylate method yields results, varying by 5 or even 10 per cent. and is, therefore, quite useless. The reason for this is no doubt the fact that these products, which are prepared with less highly concentrated acids, always contain *oxycellulose*. Since this substance is soluble in alkaline liquids, the percentage found by alkaline reagents of nitrocellulose appears too high. We shall treat of the formation of oxycellulose in a subsequent section (III, F).

III. METHODS FOR OBTAINING THE VARIOUS NITROCELLULOSES.

The first chemists who worked on nitrocelluloses adopted for cellulose the formula $C_6H_{10}O_5$, and consequently spoke of "trinitrocellulose," $C_6H_7(NO_3)_3O_5$, as the highest obtainable term, while "dinitrocellulose," $C_6H_8(NO_3)_2O_5$, was supposed to represent the composition of "soluble" nitrocellulose. The former expression is still sometimes used to denote guncotton (pyroxylin), the latter for denoting collodion cotton.

Of course it has been known for a long time past that the molecule of cellulose must be a multiple of $C_6H_{10}O_5$, but its real magnitude is not known and is not of much importance in this connection. All we need is to fix the lowest figure by which we can represent the various products obtainable by introducing NO_2 groups (nitric acid radicals) into the molecule of cellulose.

Eder¹ obtained four degrees of nitration from the highest downwards, and consequently doubled the ancient formula, as he required the molecule $C_{12}H_{20}O_{10}$ to represent all his products. Vieille,² however, obtained within the same limits a greater number of distinct products and found himself compelled to use the molecular formula $C_{24}H_{40}O_{20}$ for cellulose. This would cause the highest degree of nitration to be called "dodecanitrocellulose," in lieu of the old term "trinitrocellulose" or Eder's "hexanitrocellulose," but Vieille could not obtain this highest term at all and declared "endecanitrocellulose," $C_{23}H_{38}(NO_2)_{11}O_{20}$, to be the highest prod-

¹ Ber. d. chem. Ges., 13, 169.

² Compt. rend., 98, 132.

uct of nitration obtainable. The table given in Section II, *A*, gives the formulas and nitrogen percentages of the various stages of nitration denoted according to the $C_{n\dots\dots}$ molecule, which we adopt throughout this paper as being sufficient for representing our present stage of knowledge.

Mendelejeff¹ obtained a product containing 12.44 per cent. nitrogen entirely soluble in ether-alcohol, whose nitrogen percentage is about midway between Vieille's deca- and enneanitrocellulose. Vieille had stated that deca- was insoluble, ennea- soluble, and therefore Mendelejeff considered his soluble intermediate product as a new, individual step of nitration which would compel the adoption of a formula containing C_{48} . But as we shall see later on, there exists a soluble decanitrocellulose, and there is hence no reason whatever for making the solubility of Mendelejeff's products a criterion of its nature as an individual compound; it may very well have been a mechanical mixture of the deca- and ennea-body. I do not, therefore, at present see any reason why we should write our formulas on the basis of $C_{48\dots\dots}$, and I shall retain the basis of $C_{n\dots\dots}$ by which all our results can be satisfactorily expressed. Of course the real formula must be $nC_{n\dots\dots}$, but we may neglect the unknown value of n as immaterial for our purposes.

The lower members of the series of nitrated celluloses, up to deca-, can be obtained by means of nitric acid alone, but as even these in actual practice are always prepared by mixtures of sulphuric and nitric acids, we have almost exclusively worked with such, and we shall now proceed to discuss the conditions for obtaining the various steps of nitration.

A. On the Highest Stage of Nitration Obtainable from Cellulose.

As the older work on this subject may be considered obsolete, especially in view of the improvement of the methods for estimating the nitrogen, we may begin with the statement of Eder.² The most highly nitrated product he obtained was made by the action on cellulose of a mixture of three parts concentrated sulphuric acid and one part fuming nitric acid, and treating the product with ether-alcohol by which from 1.2 to 5.8 per cent. of soluble substances were extracted. He thus obtained a substance showing by analysis the following percentages of nitrogen: 13.91,

¹ *Moniteur Scientifique*, 1897, p. 510.

² *Ber. d. chem. Ges.*, 13, 176.

13.74, 13.82; and this he considered near enough to the percentage of 14.16, required for "hexa-" ($C_{12} \dots$ equal to our "dodeca-") nitrocellulose, to declare it to be essentially composed of this compound.

Vieille,¹ however, obtained under the same conditions a product showing only 214 cc. NO = 13.42 per cent. nitrogen, or very nearly 13.50, the percentage for endecanitrocellulose.

Vignon² attained only 213 cc. NO = 13.35 per cent. nitrogen again leading to endecanitrocellulose.

In the first series of experiments (with Weintraub) we treated each time 2.5 grams cellulose with 30 grams nitric acid (sp. gr. 1.52) and 90 grams sulphuric acid (sp. gr. 1.84) at a constant temperature of 15° during twenty-four hours; three different samples made in this way showed 13.37, 13.40, and 13.36 per cent. nitrogen. Another time, when treating the same mixtures at a temperature of 10° during ten hours, we obtained 13.39 per cent. nitrogen. That a change of temperature up to 40° or down to 0° does not produce higher nitrogen percentages, we shall see later on (Sec. III, D).

When increasing the quantity of sulphuric acid, the nitrogen percentage of the product is lowered; when decreasing it, it is decidedly, but slightly, raised as we shall see. The maximum thus obtained in this first series was 13.456 per cent. nitrogen, thus confirming Vieille's and Vignon's conclusion, that the action of a mixture of sulphuric and nitric acids leads only up to endecanitrocellulose. But their further conclusion, that no higher degree of nitration exists at all, could not be confirmed, for on applying mixtures similar to Hoitsema's³ (*viz.*, equal parts of nitrogen pentoxide and phosphorus pentoxide), we obtained up to 13.88 and 13.90, sufficiently near to the percentage for dodecanitrocellulose and far above that for endecanitrocellulose.⁴

The existence of dodecanitrocellulose has thus been confirmed both by Hoitsema and by ourselves, but it has been obtained only by the use of extraordinary reagents, not applicable in manufac-

¹ *Compt. rend.*, 95, 132.

² *Ibid.*, June 6, 1898.

³ *Ztschr. angew. Chem.*, 1898, p. 173.

⁴ H. N. Warren, *Chem. News*, 74, 239 (1896), claims to have obtained a "tetrinitrocellulose" ($C_6 \dots$), without quoting any analysis. Since he claims to have obtained this product by treating "trinitrocellulose" (guncotton) with a mixture of "equal parts by weight of commercial vitriol and phosphoric anhydride," which must have saponified and dissolved the guncotton and since he has not followed up his preliminary notice by communicating any details, we cannot treat his work seriously, any more than Hoitsema does.

turing practice. In my later experiments (with Bebie) we were more fortunate; we succeeded in getting up to the highest percentages of nitrogen by mixtures of sulphuric and nitric acids, as shown by the following table:

No.	Composition of acid mixture.			Nitrogen in product. Per cent.	Yield on cotton. Per cent.
	H ₂ SO ₄ .	HNO ₃ .	H ₂ O.		
1	60.00	27.43	12.57	13.62	173
2	62.10	25.79	12.11	13.75	174
3	62.95	24.95	12.10	13.83	175
4	63.72	25.31	10.97	13.75	175
5	64.56	24.65	10.79	13.71	175

As this work had led to the very striking result that nitrogen percentages had been reached exceeding anything previously obtained by the direct action of the mixture of sulphuric and nitric acids without extracting the products by ether-alcohol, and that with mixtures containing a comparatively large quantity of water, I thought it advisable to test this result by a new series of experiments which turned out as follows:

No.	Composition of acid mixture.			Nitrogen in product. Per cent.	Yield on cotton. Per cent.
	H ₂ SO ₄ .	HNO ₃ .	H ₂ O.		
6	68.02	25.28	5.70	13.76	...
7	64.55	26.55	8.88	13.72	173
8	63.35	25.31	11.34	13.92	173

Here, with 11.34 per cent. water in the acid mixture, we obtained 13.92 per cent. nitrogen¹ quite as high as Hoitsema and ourselves with the phosphorus pentoxide mixture, that is, close to the composition of perfectly pure dodecanitroc cellulose (= 14.16 per cent. nitrogen).

We shall later on discuss the influence of varying quantities of water on the process of nitration; in this place I wished only to prove the existence of dodecanitroc cellulose. I must, however, add that this product, as obtained by us, is not a stable compound. The sample giving 13.92 per cent. nitrogen was preserved under water for a few months and then dried and tested again; it now showed only 13.5 per cent. nitrogen. On repeating the experiments we at once obtained products up to 13.8 per cent. nitrogen but usually only the first tests yielded these values; after a few days' standing in the desiccator the percentage was only 13.5 per cent. and remained perfectly constant at this point, equal to

¹ It may be said, once for all, that there is no question of experimental errors in our analyses. Every one of our nitrogen estimations was at least made in duplicate, the discrepancies generally ranging within 0.01, very rarely up to 0.015 or 0.02 per cent. nitrogen.

endecanitrocellulose. The latter therefore appears to be the highest stable degree of nitration.

To prevent any suspicion that those extraordinarily high nitrogen percentages might be due to some nitric acid being retained in the product, every precaution was taken in washing the latter, and special check tests proved that the above could not possibly have been the case.

Special experiments were made with a view of ascertaining whether by avoiding the use of hot water in washing the products, the nitrogen percentage could be raised, but this course did not lead to more than 13.53 per cent. nitrogen and the product in question, although treated with sodium carbonate, exploded at 150° which proves it to be too unstable for any practical use.

Some further experiments showed that the proportion of sulphuric to nitric acid which, in the experiments 1 to 8, had been about 2.5 : 1, may be varied up to 3.3 : 1 and down to 2 : 1 without making a difference in the result.

No.	Composition of acid mixture.			Nitrogen in nitrocellulose. Per cent.	Yield. Per cent.
	H ₂ SO ₄	HNO ₃	H ₂ O.		
9	75.33	22.80	1.87	13.53	176
10	74.16	22.12	3.72	13.51	175
11	72.97	21.63	5.40	13.57	...
12	69.90	20.45	9.65	13.64	177
13	68.31	20.49	11.20	13.61	176
14	67.43	19.37	13.20	13.25	172
15	67.32	32.53	0.15	13.62	176.5
16	65.41	31.34	3.25	13.57	175
17	63.75	30.80	5.45	13.63	176
18	70.68	29.31	10.01	13.68	176

Those experiments further prove that by lowering the proportion of water to a minimum (which was effected by addition of fuming oil of vitriol), the percentage of nitrogen in the product was not raised, and that it is, therefore, quite useless to make the process more expensive by employing such highly concentrated acid mixtures.

B. Various Conditions to be Observed in the Nitrating Process.

The primary object of this investigation was that of establishing the conditions for obtaining with certainty the various descriptions of nitrocellulose required in commerce, from the most highly nitrated guncotton down to collodion cotton, but over and

above that to somewhat exhaustively study the process in its various bearings.

Evidently the greatest part is played in this respect by the dilution of the nitrating mixture. This may be stated in the first instance in terms of the percentage of *water* present; but the proportion of sulphuric to nitric acid must also be taken into consideration, as well as the temperature and the time occupied by the process. Lastly, it must be ascertained what part is played by that unavoidable impurity present in nitric acid, *viz.*, the lower oxides of nitrogen.

In order to attain my ultimate object it was necessary to investigate all these various conditions apart from one another, that is, varying only one of them at a time, while keeping the others as nearly uniform as the case would permit. Unless this is observed, a thorough solution of the task cannot be expected. My predecessors, with all their eminence in the field of explosives, have nothing like sufficiently fulfilled the condition just laid down. Thus Vieille¹ nitrated cotton with twelve different mixtures of sulphuric acid (sp. gr. 1.832) and nitric acid (sp. gr. 1.316) and obtained nitrocelluloses varying from 8.32 to 12.28 per cent. nitrogen. But in these experiments there were two variable magnitudes (namely HNO₃ and H₂O), and the results must depend upon both jointly. The same must be said of the numerous experiments made by Bruley.² To avoid this drawback in our case, certainly much labor was involved; several hundreds of nitrations, all followed up by careful analysis and other tests, and four years' work were expended upon this task which we shall now proceed to describe.

C. Influence of Water on the Nitrating Process.

In this series of experiments the proportion of sulphuric and nitric acids was kept practically constant, *viz.*, as nearly as possible equal (nitric acid slightly prevailing), and only the proportion of water was varied. The mixtures were prepared from "chemically pure" sulphuric acid (sp. gr. 1.83) and pure nitric acid (sp. gr. 1.50), which had been carefully freed from lower nitrogen oxides. The amount of water was varied by adding pure water, or, for the highest concentrations, by adding free sulphur trioxide in the shape of fuming sulphuric acid. The other factors, temperature,

¹ *Mem. des poudres et salpêtres*, 2, 217.

² *Ibid.*, 8, 111.

duration of action, proportion of cellulose to the acid mixture, were kept as constant as possible. The temperature was kept between 16° and 18°; the duration of action was twenty-four hours. The kind of cellulose used and the apparatus employed have been described in Section I, as well as the method of washing, drying, etc. Each experiment was (as during the whole of this work) made at least twice over, as well as the analysis of each of the products obtained, but as there was in every case a good concordance of results, I quote only the mean result of each separate variation of proportions.

The analytical methods employed are described in Section II. They extended to the nitrogen percentage, the solubility in ether-alcohol (3 ether, 1 alcohol), the yield and the behavior in polarized light.

The results of the first series of nitrations are as follows :

No.	Nitrogen. Per cent.	Soluble in ether-alcohol. Per cent.	Yield cotton. Per cent.	Acid mixture in per cent.		
				H ₂ SO ₄ .	HNO ₃ .	H ₂ O.
1	13.65	1.50	177.5	45.31	49.07	5.62
2	13.21	5.40	176.2	42.61	46.01	11.38
3	12.76	22.00	41.03	44.45	14.52
4	12.58	60.00	167.0	40.66	43.85	15.49
5	12.31	99.14	159.0	40.14	43.25	16.61
6	12.05	99.84	153.0	39.45	42.73	17.82
7	11.59	100.02	156.5	38.95	42.15	18.90
8	10.93	99.82	144.2	38.43	41.31	20.26
9	9.76	74.22	146.0	37.20	40.30	22.50
10	9.31	1.15	138.9	36.72	39.78	23.50
11	8.40	0.61	131.2	35.87	38.83	25.30
12	6.50	1.73	34.41	37.17	28.42

These results have been plotted on the accompanying diagram, the upright lines showing on one side the number of cubic centimeters of NO evolved per gram of the product, on the other side the nitrogen percentage of the same, and the horizontal lines showing the percentage of water in the acid mixture. It appears that the single results (marked by circlets) arrange themselves in a very regular curve which allows of foreseeing the nitrogen percentage of the product for the varying proportions of water in the acid mixtures employed for nitration.

As might be expected, and as is especially shown by a glance at the third column of the preceding table (the solubility in ether-alcohol), the products obtained mostly, were not chemically pure individual compounds, but mixtures of various stages of nitration.

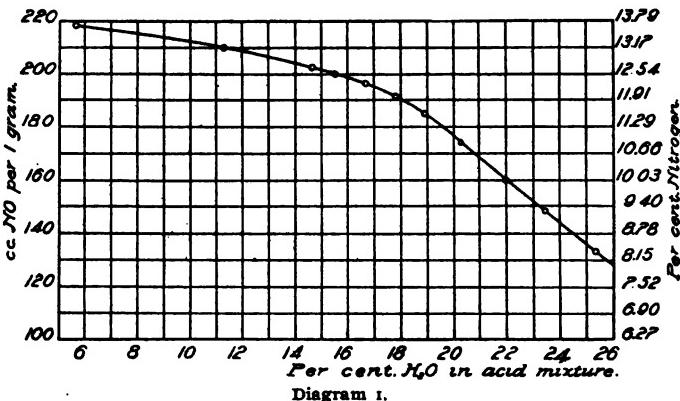


Diagram I.

The solubility in ether-alcohol may be made use of for at least a partial separation of the products of nitration. Of course, both the soluble and insoluble portions might be assumed to consist of a mixture of various nitrocelluloses, but frequently their nitrogen percentage shows them to be of uniform nature. Where either the soluble or the insoluble portion amounted but to a few per cent. of the whole, lack of material precluded their separate investigation, and in these cases, only the prevailing portion was separately analyzed and the nitrogen percentage of the portion indirectly estimated by the following mode of calculation.

Suppose we have directly estimated the nitrogen percentage of the insoluble portion, a denoting the nitrogen percentage of the entire mixture obtained by nitration and c the percentage solubility in ether-alcohol. We shall learn the nitrogen percentage d of the soluble portion by the formula

$$d = \frac{100(a-b) + b.c}{c}.$$

If, on the other hand, the nitrogen percentage d of the soluble portion is known, we learn the percentage b of the insoluble by the formula

$$b = \frac{100a - dc}{100 - c}.$$

Considering that the estimation of solubility is not a very accurate operation, especially in the case of low solubilities, we cannot ascribe a very high degree of accuracy to these indirect estimations of the nitrogen percentage, but they will, at all events, sufficiently elucidate the progress of nitration.

We shall now discuss the single results a little in detail. No. 1 shows a product of strikingly high nitrogen percentage, exceeding the highest attained by Vieille. This product was obtained with an acid mixture containing 5.62 per cent. water; we have seen in Section III, A, that even higher percentages of nitrogen can be obtained with mixtures containing rather more water, but also more sulphuric acid than was employed in this case. The nitrogen percentage increased but very little by extraction with ether-alcohol, *viz.*, to 13.67, that of the soluble portion being calculated as 12.54 per cent.

An increase of the percentage of water to about 11 per cent. caused a slight diminution of the nitrogen percentage. In Section III, A, we have seen that with the same percentage of water, but with more sulphuric acid, the maximum percentage of nitrogen was attained. The insoluble portion of No. 2 contains 13.37 per cent. nitrogen and is, therefore, practically equal to decanitrocellulose. The soluble portion is calculated to contain 11.35 per cent. nitrogen.

The nitrogen percentage of No. 3 (12.76) is exactly like that of decanitrocellulose (theoretically 12.78); but its partial solubility shows that it was not a chemical individual, and its nitrogen content only accidentally agreed so well with decanitrocellulose (Eder's pentanitrocellulose). It could be split up into 22 per cent. of octonitrocellulose, with 11.10 per cent. nitrogen (theory 11.13) and 78 per cent. of another substance, showing by calculation as above 13.23 and by actual analysis 13.26 per cent. nitrogen. This is a strong warning against drawing conclusions on the solubility and other properties of technical nitrocellulose from its accidental percentage of nitrogen, which subject we shall have to mention again further on.

The difference between the degree of nitration of the soluble and insoluble components of the samples hitherto discussed is no doubt caused by the dilution of the acid mixture taking place during the nitrating process, firstly by the positive formation of water, secondly by the abstraction of nitric acid. Since these experiments show that a difference of a few per cent. of water may produce greatly differing stages of nitration, we understand why, during the nitrating process, where there is a chemical production of free water, various nitrocelluloses must be produced. The variations must be less prominent, the greater

the proportion of acids to that of the cotton, and the lesser consequently the absolute changes in the composition of the acid mixture. This explains why the proportion between the quantity of cotton and that of the acid mixture is an important factor in the process.

Combining the knowledge to be derived from the experiments hitherto discussed (made with about equal quantities of sulphuric and nitric acids and water up to 11 per cent.) with those described in the preceding section (where the ordinary mixture of 3 sulphuric to 1 nitric acid was applied with varying quantities of water), we arrive at the conclusion that *in order to make gun-cotton of a high percentage of nitrogen it is quite unnecessary to employ acid mixtures containing only a few per cent. of water.* With the acid proportion 1 : 1 it is permissible to go up to 10 per cent. water, with 3 sulphuric to 1 nitric acid even *up to 12 per cent. water, and consequently to work with much cheaper acids than is usually done.*

From Professor Will's paper on the stability of nitrocellulose which I have received at the last moment before closing this paper, and which will be referred to later, I notice that under otherwise equal conditions and equal relation between sulphuric and nitric acid, *the rapidity with which nitrogen is given off from the nitrocellulose at a temperature of 135° (which he considers to be the surest test for the stability of nitrocelluloses) decreases with the increased percentage of water in the nitrating acid.* The same amount of decomposition as is brought about in fifty-five minutes with a mixture containing 4 per cent. water, required 255 minutes with a mixture containing 9 per cent. water. *This greatly increased stability is another strong argument for the recommendation which I have derived from my experiments, to employ acid mixtures containing more water than has been hitherto the custom.*

No. 4 of the above series is an intermediate mixture; with No. 5 we reach the series of completely soluble products, that is, the *collodion cottons.* As the curve shows, the influence of the increase of water now becomes much stronger. Over 18 per cent. water the nitrogen percentage quickly decreases with the increase of water. The group of entirely soluble nitrocelluloses, with from 12.31 to 10.93 per cent. nitrogen, is obtained by acid mixtures ranging between 16.6 and 20.3 per cent. water. Between

Nos. 7 and 8 we should find the typical collodion cotton, *viz.*, octonitrocellulose, with 11.13 per cent. nitrogen, and by interpolation on the curve we find the corresponding amount of water in the acid mixture = 19.5 per cent. This conclusion was confirmed by actual experiment. An acid mixture containing the same proportions of sulphuric and nitric acids as employed above, and 19.42 per cent. water, yielded *practically pure octonitrocellulose*, and we have thus shown how to obtain with all certainty this product which is of such great technical importance, and which is usually assumed to be somewhat difficult to manufacture with regularity.

I must here interpose some remarks on a paper published by Wyss-Naef¹ upon the preparation of collodion cotton, to be employed in the manufacture of vegetable silks at the Besancon factory. According to him this collodion cotton is made by treating cotton during four to six hours with a mixture of 85 parts sulphuric and 15 parts fuming nitric acid (sp. gr. 1.52). He does not expressly speak of the concentration of the sulphuric acid, but he must evidently mean the ordinary concentrated oil of vitriol (66° Baumé), for he speaks of the strong attraction of the acid mixture for water, and moreover nobody would for a technical process employ such costly nitric acid as that of 1.52 specific gravity, to mix with dilute sulphuric acid, instead of the much cheaper mixture of concentrated sulphuric and weaker nitric acid.

Wyss-Naef's statements have been reproduced without criticism in a recently published book by Dr. Süvern, "Die künstliche Seide."

It would have been an extremely valuable service to the industry of collodion cotton if the detailed descriptions of Wyss-Naef on the process employed at Besancon could be accepted as correct, although it would be an almost unexampled instance of generosity on the part of the owners and managers of that factory to make such a present of their hitherto secret process to their competitors in trade. Unfortunately this is not the case. In the first paper published in 1899 by Weintraub and myself we had already shown that when carefully following the instructions of Wyss-Naef even after three days some raw cellulose was left behind, that the final product contained 12.74 per cent. nitrogen, that it differed entirely from the published description in its

¹ *Ztschr. angew. Chem.*, 1899, p. 469.

behavior under the polarization microscope, and that it contained only 19 per cent. of matter soluble in ether-alcohol. Then we publicly challenged Mr. Wyss-Naef to clear up these contradictions, but received no answer.

Looking at the importance of this matter, I repeated with Bebie the operation as prescribed by Wyss-Naef, this time at slightly raised temperatures, as we had learned that such are employed at the factories of vegetable silk. The following figures show that by this, only some time was saved, as a matter of course, but that the products are just as little "soluble" nitrocellulose as in our former experiments.

Temperature.	Duration of nitration. Hours.	Nitrogen. Per cent.	Solubility Per cent.	Yield Per cent.
30°	4	12.53	17.14	160.2
40°	7	13.12	15.54	143.1

There was no unchanged cotton left behind. In the polarized light the fibers showed a faint steel-blue color.

I must, therefore, assume until further explanations, that the prescriptions of Wyss-Naef on the manufacture of collodion cotton are entirely untrustworthy, and I must adhere to the prescription given above from the experiments made in my own laboratory.

We now resume the discussion of these experiments. Below 10 per cent. nitrogen the solubility of nitrocellulose quickly decreases. The products from hexanitrocellulose downwards are insoluble, as previously found by Vieille. The soluble hexa- and tetrinitrocelluloses, obtained by Eder with very hot acid mixtures, or by the action of alcoholic potash on more highly nitrated products are evidently of quite a different nature, since no cellulose could be regenerated by means of ferrous chloride, and they must be considered as not being nitrated celluloses at all, but nitric esters of other carbohydrates.

If the percentage of the acid mixture attains 25 per cent. or more, no complete nitration can be effected by an action of twenty-four hours; in No. 12, unchanged cotton was left, even after three days' action, to the amount of 4.1 per cent.; the nitrated portion would then contain 6.78 per cent. nitrogen, and consists of tetrinitrocellulose. But as mentioned in Section II, the estimation of the unchanged cellulose and consequently that of the nitrogen percentage in the other portion, can be only approximate in such cases.

In the presence of more water the nitration becomes less and less complete. In the beginning there is still some nitration, later on, only oxycellulose is formed, as shown by the entire or partial solubility in dilute alkali, precipitation from the solutions by acids or alcohol, intense coloration with basic coloring-matters, reduction of Fehling's solution and formation of compounds with phenylhydrazine.

The *morphological structure* of the products is strongly altered by an increase of water in the acid mixtures. Up to 15 per cent. water the original structure is preserved. At 18 per cent. water, the fibers appear somewhat contracted and the characteristic twist of cotton fiber is lost. With more water the fibers appear to be torn open and disaggregate into small particles which get felted into globular masses. This destructive action is at its maximum with 23 or 25 per cent. water; by more dilute acid mixtures the fibrous structure is much less affected, but here also by prolonged action the fibers are split up into smaller elements.

A further series of tests was made to ascertain whether gun-cotton, made with acid mixtures containing from 8 to 11 per cent. water, as recommended by me in consequence of our investigations, might be *less resistant to boiling water* than those made with more concentrated acids. This did not seem very likely, but still it had to be examined.

For this purpose two nitrations were made simultaneously: (1) with the usual mixture (69.14 H₂SO₄, 23.91 HNO₃, 6.07 H₂O, 0.88 N₂O₄), and (2) with a mixture containing 63.64 H₂SO₄, 25.25 HNO₃, 10.82 H₂O. Both were treated exactly in the same way with cold, hot, and boiling water, and were tested for nitrogen percentage and explosiveness. The following were the results, proving that guncotton made according to our prescription does not lose any more nitrogen on boiling with water than such made with more concentrated acids.

No.	Kind of treatment.	Product 1.		Product 2.	
		Nitrogen. Per cent.	Ex- plosion.	Nitrogen. Per cent.	Ex- plosion.
1.	Washed one-half day cold, one day hot water.....	13.45	161° 3'9"	13.64	158° 3'5"
2.	Washed one-half day cold, three days hot.....	13.48	170° 4'40"	13.49	163° 4'30"
3.	Washed one-half day cold, one and one-half days hot, boiled two hours (no acid reaction in water)	13.47		13.50	
4.	The same boiled another five hours	13.36		13.45	

Product 2 behaves in the washing process exactly like 1; there is a trifling loss of nitrogen, which remains always slightly above 1, but this difference does not seem to be of any importance, no more than the slight difference in explosiveness.

Of course, only more extended experiments on the large scale could absolutely decide these questions, and the question of ballistic differences could not even be approached by us.

D. Influence of Temperature.

The experiments described in Section III, C, were all made at the ordinary temperature and lasted twenty-four hours. The question now arises how the process is affected by varying the temperature of the nitrating process. This was separately studied for the case of guncotton and that of collodion cotton.

For guncotton as nearly as possible 2.5 grams of cotton were nitrated with a mixture of 30 grams nitric acid (sp. gr. 1.52), and 90 grams sulphuric acid (sp. gr. 1.84). The duration of the process could not very well be raised above seven hours, as the temperature had to be watched throughout the process. The results are quoted in the following table. The "yields" refer to 100 parts of cotton employed; the "loss of cellulose" is calculated per cent. of cellulose employed from the formula: $100 - b(1 - 0.0201a)$, where b is the yield from 100 parts cellulose, and a the number of cubic centimeters of NO given off from 1 gram nitrocellulose.

Temperature.	Nitrogen. Per cent.	Yield. Per cent.	Loss of cellulose. Per cent.	No.
0° { ½ hour	10.71	152.29	trace	1
	13.19	173.29	trace	2
10° 7 hours	13.37	175.78	3
15° 7 hours	13.38	175.61	4
19° { ½ hour	12.72	166.14	5
	13.39	175.56	6
40° { ½ hour	13.07	172.32	trace	7
	13.06	169.62	1.61	8
60° { ½ hour	13.08	169.18	1.95	9
	13.07	162.05	5.67	10
80° { ½ hour	13.07	161.23	6.52	11
	13.12	125.17	27.45	12
3 hours	13.12	81.52	52.76	13

From this the following conclusions may be drawn:

1. *With the rise in temperature the speed of the process increases rapidly.* At 0° the nitrogen percentage reached after half an

hour is only 10.71, at 19° it is increased to 12.72, at 40° to 13.07 (which is the highest attainable at this temperature), and at 80° this is effected in a quarter of an hour.

2. *The nitrogen percentage of the product sinks a little when passing from ordinary temperatures (10° to 19°) to 40° (viz., from 13.39 to 13.06 per cent. nitrogen) but remains practically at the same figure when nitrating at 60° or 80°.*

3. *The principal influence of the temperature of nitration is exerted upon the yield, which, when passing from the ordinary to higher temperatures, constantly falls.* This does not take place by direct solution of cellulose proper; first the cellulose itself is rapidly nitrated, and the nitrocellulose formed is thereupon partially dissolved, all the more quickly, the higher the temperature.

4. *By nitrating at higher temperatures the structure of the cellulose is changed.* It becomes short and fragile; that obtained at 60° or 80° is a finely fibrous powder after drying.

If the proportion of sulphuric to nitric acid is larger than the usual 3 : 1, the loss of yield and the solubility on raising the temperature of nitration are even more strongly pronounced. With 11 sulphuric to 1 nitric acid an increase by a few degrees of temperature has the same effect as 20° or 30° with the acid proportion 3 : 1.

It is also necessary for each temperature to find out the most suitable duration of the action of the acids. At the ordinary temperature there is a wide margin in that respect, but at higher temperatures we observe that the nitrogen percentage rises at first and on longer action decreases again. Thus the same acid mixture (3 : 1) at a temperature of 32° produced the following nitrogen percentages :

Time of action. Minutes.	Nitrogen. Per cent.
5	13.27
15	13.44
30	13.47
60	13.50
120	13.40

Hence the maximum was reached in this special case after an hour's action.

Looking at all circumstances, we conclude that in manufacturing guncotton the ordinary process of not exceeding a tempera-

ture of 25° during the nitration is right. We thus obtain a maximum percentage of nitrogen and a maximum yield within a reasonable time.

We now pass to *collodion cotton*, where a somewhat higher than the ordinary temperature is frequently employed in practice. Here the mixture of acids was employed which is mentioned in Section III, C, Experiment 7; viz., 38.95 H₂SO₄, 42.15 HNO₃, 18.90 H₂O. The results were :

No.	Temperature.	Time of nitration. Hours.	Nitrogen. Per cent.	Solubility in ether-alcohol. Per cent.	Yield. Per cent.
14	17°	4	11.50	95.60	155.1
15	17°	24	11.59	99.81	156.2
16	40°	4	11.49	99.58	148.1
17	60°	1/4	11.46	99.71	146.7
18	60°	4	10.81	99.82	152.0

At 17° the *nitration* is practically completed in four hours ; the yield is rather larger than at 40° , but the *solubility* was not quite so good, the product dissolving both more slowly and less completely.

At 40° the solubility is excellent, the yield decidedly less, and the nitrogen percentage is normal.

At 60° about the same result was accomplished after a quarter of an hour; after this the nitrogen percentage was lower. The structure of the cotton is to a great extent destroyed at this temperature. Although Experiment 4 showed that about as good a percentage and solubility can be attained at 60° in one-fourth hour, as at 40° in four hours, the change of structure seems to have ulterior consequences, for, as I am informed from reliable practical authority, the collodion cotton made at such high temperatures does not yield vegetable silk fit for spinning. Probably simultaneously with the change of morphological structure the cellulose molecule is also changed.

Our conclusion is that about 40° is the best temperature for obtaining collodion cotton, as this gives a maximum of solubility within a reasonable time (four hours), with no change of structure and comparatively little danger of overdoing the action.

E. Influence of Varying the Proportion of Sulphuric Acid to Nitric Acid.

The only observation I have found in the above respect is by Vieille¹ : "A great excess of sulphuric acid influences especially the speed of the reaction which is greatly lessened."

The first series of experiments was made in cooperation with Weintraub. Each time 2.5 grams cotton were taken with 30 grams nitric acid (sp. gr. 1.52) and varying quantities of sulphuric acid; only in the cases where very little or no sulphuric acid at all was employed the quantity of nitric acid had to be increased, in order to soak the cotton thoroughly well. The experiments were made at the ordinary temperature, which at that time was from 19° to 20° and was kept quite constant during the shorter experiments, but became somewhat lower during the nights, reaching 15° and even 13°. Section III, D, shows that this would have no perceptible influence on the results in the case of mixtures containing up to 3 sulphuric to 1 nitric acid. Special experiments, described in our German paper, show that the difference between 13° and 20° is perceptible when the proportion of sulphuric to nitric acid is 7 : 1 and more so when it is 11 : 1, but not to the extent of altering the conclusions to be drawn.

TABLE I.

Nitric acid.	Sulphuric acid.	One-half hour.		Twenty-four hours.		Three days.	
		Nitrogen. Per cent.	Yield. Per cent.	Nitrogen. Per cent.	Yield. Per cent.	Nitrogen. Per cent.	Yield. Per cent.
I	0	12.58	162.75	12.62	163.32
I	1	12.66	165.02
I	2	13.45	175.69	13.44	175.77
I	3	13.42	175.22
I	4	13.36	174.56	13.39	174.75
I	5	13.23	174.14	13.32	175.98
I	6	12.72	166.14	13.40	176.44	13.38	175.55
I	7	12.72	166.14	13.40	176.44	13.38	175.55
I	8	13.20	175.12
I	9	8.14	130.88	13.10	166.60
		(25.44 unchanged cellulose.)					

TABLE II.

Nitric acid.	Sulphuric acid.	Three days.			Eight days.			Fifteen days.			Thirty days.		
		Nitrogen. Per cent.	Yield. Per cent.	Unchanged cellulose. Per cent.	Nitrogen. Per cent.	Yield. Per cent.	Unchanged cellulose. Per cent.	Nitrogen. Per cent.	Yield. Per cent.	Unchanged cellulose. Per cent.	Nitrogen. Per cent.	Yield. Per cent.	Unchanged cellulose. Per cent.
I	6	12.63	162.40	0.85	12.74	169.80	none
I	7	10.86	151.60	10.46
I	8	10.88	144.62	10.7	11.70	152.0	4.48
I	9	77.4	120.11	much
I	10	5.43	65.0	41.12

The conclusions arrived at from that series were as follows :

1. *With the increase of the quantity of sulphuric acid the speed of the process decreases rapidly.* Up to equal parts sulphuric and nitric acid the final stage of nitration is reached in half an hour. With acids in the proportion of 3 : 1 the first half hour brings us only to 12.72 per cent. nitrogen, the final stage being 13.40 per cent. nitrogen ; with 8 : 1 the final stage is not reached even after eight days, and only after thirty days is it equal to 11.70 per cent. nitrogen.

2. *The maximum of nitrogen percentage of the products is obtained if the proportion of sulphuric to nitric acid is not less than $1\frac{1}{4} : 1$, and not more than 3 : 1.* Above 3 : 1 the nitrogen percentage falls first slowly, then more rapidly, but we must not overlook that with a very great excess of sulphuric acid a difference of a few degrees of temperature equally affects the result very seriously. (Compare the more detailed investigation of this point further on.)

3. *Above a certain proportion of sulphuric to nitric acid (apparently 8 : 1) the final product always contains unchanged cellulose.*

4. *An excess of sulphuric acid affects also the structure of nitrocellulose.* When employing pure nitric acid or up to 0.5 sulphuric to 1 nitric acid, the fibers contract and become more resisting. Beyond 7 : 1 the cellulose fibers are destroyed, and on drying fall into a finely fibrous powder.

These experiments had shown that with nitric acid alone the nitration cannot be driven beyond decanitrocellulose. *Collodion cotton*, consequently, might be prepared with nitric acid alone, but practically, this is never employed, since by the addition of sulphuric acid a great saving of nitric acid and of time is effected. There is not very much known about the best proportions of acids for preparing collodion cotton ; the published statements vary from 1 sulphuric to 1 nitric acid up to 6 : 1, and are partly decidedly misleading (compare above sub C). We have in Section III, C, shown the results obtained with that proportion of acids which is probably the best for collodion cotton ; viz., about 1 : 1, with from 18 to 20 per cent. water in the mixture. I now give the results of experiments (with Bebie), intended to study more completely the conditions of making collodion cotton when varying the quantities of the acids and the proportions of water.

No.	Nitrating mixture.				Product.			Proportion of HNO ₃ in acids to 1 cellulose.
	Parts H ₂ SO ₄ to 1 part HNO ₃ .	H ₂ SO ₄ , Percent.	HNO ₃ , Per cent.	H ₂ O, Per cent.	Nitrogen, Per cent.	Solubility in ether-alcohol, Per cent.	Yield, Per cent.	
1	3	62.18	21.91	15.91	13.21	3.20	174	30
2	3	61.53	20.02	18.45	12.42	98.70	160	30
3	3	60.30	19.71	19.99	11.72	99.28	157	30
4	3	58.88	19.60	21.52	10.96	99.50	148	30
5	3	59.77	20.94	19.29	11.74	99.98	159	12
6	3	58.34	20.62	21.04	10.90	99.20	149	12
7	3.8	63.84	16.96	19.20	12.08	163	30
8	3.8	62.52	16.46	21.02	11.23	153	30
9	3.8	63.84	16.96	19.20	11.76	156	12
10	3.8	62.52	16.46	21.02	10.99	151	12
11	5	67.60	13.66	18.74	12.43	167	30
12	5	66.37	13.04	20.59	11.66	148	30
13	5	64.85	14.90	20.25	10.53	140	8
14	5	64.11	13.62	22.27	9.35	8

No. 1, prepared with too little water, is still a guncotton. No. 2 is evidently identical with Mendelejeff's "pyrocollodion," both as to its nitrogen percentage and its solubility. The remaining samples are collodion cotton of various nitrogen percentages and various yields.

The differences between this series and the experiments described

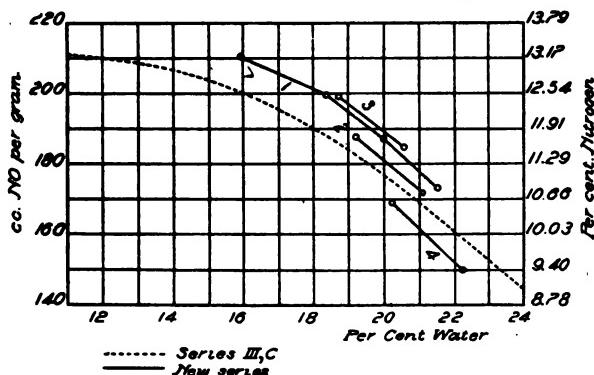


Diagram 2.

in Section III, C, where the proportion of acids was 1 : 1, is made very clear by the diagram appended here, in which the former series (with acids = 1 : 1) is represented by the dotted line; the full curve 1 shows the results obtained with sulphuric to nitric acid = 3 : 1; total acids = 30 to 1 cellulose; curve 2 refers to the same proportion, but 12 acids to 1 cellulose; curve 3 refers to

the acid proportion of 5 sulphuric to 1 nitric acid, and a total of 30 acids to 1 cellulose; curve 4 refers to the same proportion of acids, but 8 total acids to 1 cellulose.

We see that the proportion of water being equal, an increase of the sulphuric acid from the proportion 1 : 1 to 3 : 1 causes an increase of 0.63 per cent. nitrogen in the product if the proportion of total acids is 30 to 1 cellulose, and an increase of about half as much, say 0.3 per cent. nitrogen, if the total acids are 12 : 1 cellulose. When increasing the proportion of water, the nitrogen percentage decreases quite as much with the acid proportion of 3 sulphuric to 1 nitric acid, as with 1 : 1.

The acid proportion 3.8 : 1 yields practically the same results as 3 : 1, and no curve has been drawn for this reason.

With the acid proportion 5 : 1 there was a very slight rise of nitrogen percentage in comparison with 3 : 1, but only if we employ 30 acids to 1 cellulose; if this quantity is lowered to 8 acids to 1 cellulose, the nitrogen percentage of the product strongly decreases. In the former series of experiments there had been a slight *decrease* of nitrogen with this proportion of acids; evidently there is not much difference either way.

All these experiments were made at the ordinary temperature and the nitration lasted twenty-four hours. Experiments made with the same acid proportions (1 : 3, 1 : 3.8, 1 : 5) at 35° showed that exactly the same results could be obtained at that temperature in two hours.

In the next following series of experiments, it was my aim to *keep the proportion of nitric acid to that of water perfectly constant and to vary only the sulphuric acid proper*. For that purpose, we started with nitric acid (sp. gr. 1.40) containing 184 parts HNO₃ to 100 parts H₂O, and added to this varying quantities of concentrated sulphuric acid, but as the latter contained 5.09 H₂O to 94.91 H₂SO₄, this 5 per cent. of water was always compensated by adding the calculated quantity of stronger nitric acid (sp. gr., 1.50), so that the proportion of HNO₃ to H₂O remained always as nearly as possible the same. Of course, the acid mixtures were always analyzed before use.

The experiments were made at the ordinary temperature and lasted 24 hours.

Up to 33 per cent. H₂SO₄, there was always unchanged cellulose left. On trying to estimate this it was found that the method

described in Section II, *F*, did not yield very reliable results, owing to the formation of oxycellulose. I shall, therefore, not quote these experiments in detail, but describe only their general character.

Even nitric acid of 1.4 specific gravity by itself causes a partial nitration, but about 63 per cent. cellulose remained unchanged, no oxycellulose being formed here. The product, as a whole, contained 1.49 per cent. nitrogen, and the nitrated portion alone by calculation 4.00 per cent. nitrogen, which corresponds to *dinitrocellulose* ($C_{24} \dots$). As this product has never been obtained elsewhere, many attempts were made to isolate it by the action of solvents, or to prepare it otherwise in a purer state, but in vain.

By addition of 5 per cent. H_2SO_4 , some oxycellulose was formed. The product contained about 58 per cent. unchanged cellulose, and 2.15 per cent. nitrogen; *trinitrocellulose* ($C_{24} \dots$) would contain 5.36 per cent. nitrogen. Here, as well, it was not found possible to isolate the products as a chemical individual.

I omit a description of the next experiments, with more sulphuric acid, where the mixture of nitrocellulose with oxycellulose and cellulose could not be properly unraveled, and I pass on to those where products free from unchanged cellulose were obtained, employing about 25 parts by weight of nitric acid and 14 parts water to 1 cellulose, the quantity of sulphuric acid being varied.

No.	Acid mixture.			Product.		
	H_2SO_4 . Per cent.	HNO_3 . Per cent.	H_2O . Per cent.	Nitrogen. Per cent.	Solubility. Per cent.	Yield. Per cent.
15	41.86	35.82	22.32	9.27	14.22	134
16	38.47	40.19	21.34	10.32	92.30	142
17	40.83	38.72	20.45	10.76	98.24	151
18	42.92	37.40	19.68	11.02	98.90	153
19	48.03	34.18	17.79	12.23	99.58	155
20	49.37	33.38	17.25	12.77	99.82	166
21	50.71	32.50	16.79	13.02	99.32	165
22	52.81	31.27	15.92	13.11	7.65	167
23	54.92	30.06	15.02	13.45	2.63	173

The product of No. 15 was treated by a solvent indicated to me by Dr. Brönnert as acting upon nitrocelluloses below octonitrocellulose; *viz.*, a solution of 4 parts calcium chloride in 100 parts alcohol of 95 per cent. This solvent extracted in the cold about 10 per cent., on boiling with reflux cooler another 35 per cent., but the remaining product contained almost exactly as much nitrogen as the raw product; *viz.*, 9.32 per cent. The portion in-

soluble in ether-alcohol is practically pure *hexanitrocellulose* (= 9.17 per cent. nitrogen).

Nos. 16, 17, 18, and 19 belong to the group of collodion cottons and call for no special remark. By a slight increase of sulphuric acid we get to a product, No. 20, having the exact composition of decanitrocellulose (theoretically 12.78 per cent. nitrogen), and still *completely soluble in ether-alcohol*. Even No. 21, with 13.02 per cent. nitrogen, is still completely soluble. This is a cogent proof that various forms of decanitrocellulose exist; for both Vieille and myself (with Weintraub) had previously obtained *insoluble* decanitrocellulose (compare Section III, G). We then had worked with more concentrated acids; now, with more water, a *soluble* decanitrocellulose was obtained, which Eder had also prepared before.

Sir H. E. Roscoe, on the occasion of the "Cordite action," had also been able to make both soluble and insoluble nitrocellulose containing 12.8 per cent. nitrogen. H. C. Aspinwall¹ mentions that he obtained soluble nitrocellulose with 12.91 per cent. nitrogen.

These facts are of technical importance; for in the manufacture of blasting gelatine and other blasting agents it is very important to employ *products soluble in ether-alcohol, with a maximum of nitrogen*. A discussion at a meeting of the New York Section of the Society of Chemical Industry² shows that the conditions for obtaining such products are not generally known, and probably they have been laid before the public for the first time by this present investigation.

By further increasing the quantity of sulphuric acid the solubility suddenly dropped to a minimum, with a very slight rise of nitrogen percentage. The last experiment, No. 23, led to practically pure *endecanitrocellulose*, that is the best guncotton obtained in ordinary manufacturing practice. This was done with a remarkably high dilution of 15 per cent. water in the acid mixture, while in practice much more concentrated acids are generally employed. It was just this circumstance which led us to further investigate the conditions for reaching the highest possible state of nitration, as described in Section III, A, where we have seen that these highly nitrated products were

¹ *Moniteur Scientifique*, 1900, p. 829.

² *J. Soc. Chem. Ind.*, 1900, p. 315.

reached with 11 to 12 per cent. water in the acid mixture, while mixtures with 6 down to 1½ per cent. water only led to endecanitrocellulose or little beyond.

Before closing this paper, I see from a paper by Professor Will just received, printed for private circulation, on the stability of nitrocelluloses (compare Section III, C and G) that under equal conditions *an increase of the sulphuric acid in the acid mixture accelerates the decomposition of the nitrocellulose.* Up to 3 sulphuric to 1 nitric acid this acceleration is but slight, but it increases rapidly beyond that limit. This corroborates the conclusion at which I had arrived by my own experiments; viz., that for manufacturing guncotton of a high percentage of nitrogen it is advisable to work with a proportion of three parts sulphuric to one of nitric acid, but no more than this quantity of sulphuric acid. Thus the maximum of nitrogen percentage and nearly the maximum of stability will be attained (*i. e.*, if the advice is followed given at the conclusion of Section III, C, concerning the proportion of water).

For the manufacture of collodion cotton there is no reason for exceeding the proportion of equal parts of sulphuric and nitric acids, with from 19 to 20 per cent. water in the mixture.

F. Formation of Oxycellulose in the Nitrating Process.

I have mentioned above that with more dilute acid mixtures oxycellulose is evidently formed, and probably nitrooxycellulose is present as well. Previously Brönnert¹ and Vignon² have noticed this, and they assert that also with concentrated acids oxycellulose is formed. This question seemed to require further elucidation.

Vignon founded his opinion on the observation that both nitrated cellulose and nitrated oxycellulose reduce Fehling's solution, and that this is independent of the degree of nitration. It is however a fact that other, probably more characteristic, reagents for oxycellulose do not act in the same way. The usual reaction for oxycellulose is its behavior towards basic coloring-matters, especially methylene blue, and this was applied to the case in question.

For each test 0.5 gram of the product to be examined was heated on the water-bath with 150 cc. of a 5 per mille solution of

¹ *Bulletin de Mulhouse*, 1900.

² *Compt. rend.*, September 10, 1900.

methylene blue during an hour, and, after cooling, 100 cc. were compared with 100 cc. of the original solution in a Lummer-Brod-huhn colorimeter in order to ascertain the loss of coloring-matter. The following results were obtained :

Nitrogen in nitro-cellulose. Per cent.	Methylene blue, fixed by 1 gram. Gram.
0 (pure cellulose)	0.0012
13.65	0.0010
13.21	0.0009
12.76	0.0011
12.05	0.0021
10.93	0.0036
8.40	0.0120

This shows that the products obtained with concentrated acids contain no oxycellulose, but those obtained with dilute acids did contain such, and further tests confirmed this. The same result was obtained with Schiff's reagent for aldehydic groups (a solution of fuchsine decolorized by sulphuric acid).

G. Solubility of Nitrocelluloses in Ether-Alcohol.

I have had to refer on many previous occasions in this paper to the solubility of nitrocelluloses in ether-alcohol, by which we understand a mixture of 3 parts ether with 1 part alcohol. Here I quote in the first instance some experiments made specially with a view of deciding the behavior of decanitrocellulose in this regard.

By the action of nitric acid (sp. gr. 1.5) mixed with only 1/10 of its weight of sulphuric acid (sp. gr. 1.84), during twenty-four hours, a product was obtained containing 12.76 per cent. nitrogen ; that is, practically pure decanitrocellulose. This product was as good as insoluble in ether-alcohol to which it yielded only 2.1 to 2.25 per cent. The microscope showed a very uniform structure ; all fibers flashed up blue in polarized light. Hence, this product was most probably really an *insoluble* decanitrocellulose.

By nitrating as Vieille had done; with pure concentrated nitric acid, the same result was obtained.

When increasing the proportion of sulphuric to nitric acid over 3 : 1, the nitrogen percentage very slowly falls, but the *solubility in ether-alcohol rises*.

By the action of a mixture of 6 sulphuric to 1 nitric acid during

fourteen days a product was obtained with 12.78 per cent. nitrogen, precisely like the percentage of decanitrocellulose, but it contained 19.17 per cent. soluble and 80.83 per cent. insoluble matter, the latter showing 13.08 per cent. nitrogen.

In our later experiments we obtained (Sec. III, C, No. 3) by the action of 41.03 per cent. sulphuric acid, 44.45 per cent. nitric acid, 14.52 per cent. water a product with 12.76 per cent. nitrogen of which 22 per cent. was soluble. I have pointed out before, that these results prove the product to have been mixtures of various degrees of nitration.

But in Section E, No. 20, we find a product with the exact percentage of decanitrocellulose, *completely soluble* in ether-alcohol (produced by the action of 49.37 per cent. sulphuric, 33.38 per cent. nitric acid, and 17.25 per cent. water).

All this, together with the results of Roscoe and of Aspinwall, proves that it is wrong to put the question in this way : "Is a nitrocellulose of 12.78 per cent. nitrogen, that is of the percentage of decanitrocellulose, soluble in ether-alcohol or not?" We have seen that by varying the proportions of acids and water in the nitrating mixture, quite a number of products may be obtained possessing the above nitrogen percentage, but varying in solubility from 0 to 100 per cent. ; and evidently constituting quite different mixtures of such compounds.

A fortiori we cannot acknowledge as true decanitrocellulose the products obtained by Eder when treating for an hour and thus *dissolving* collodion cotton in nitric acid (sp. gr. 1.40) at 60°, which products contained 13.02 and 12.84 per cent. nitrogen and were easily soluble in ether-alcohol. By such energetic treatment as is produced by solution in hot nitric acid, the cellulose molecule must be thoroughly altered. When repeating Eder's experiments we obtained, by slightly changing the temperature, the time, and the quantity of acid, all sorts of products varying between 9.84 and 12.4 per cent. nitrogen ; but we did not reach 12.78 per cent. The solution at first yields a precipitate with sodium carbonate ; by longer digestion this property is lost. It then cannot contain either cotton cellulose or a nitric acid ester of this, as both would be precipitated by sodium carbonate. Evidently by the above treatment a variety of carbohydrates and their nitration products is formed, among which there may be some soluble compound of the percentage composition of decanitrocetyl-

lulose, but quite different from the compound prepared in the usual way.

In this respect it is most interesting to note that it is possible to prepare *nitrocelluloses soluble in ordinary alcohol* (95 per cent.). When making the last-mentioned experiments (with pure nitric acid), we frequently got products containing 11 to 11.16 per cent. nitrogen which dissolved in alcohol with the greatest facility. This is the composition of *octonitrocellulose* (11.13 per cent. nitrogen), which according to Eder should be *insoluble* in alcohol! These products are also soluble in concentrated nitric acid. Evidently they belong to a different class of compounds.

But it is even possible to obtain a compound of the composition of *decanitrocellulose*, which is *soluble in alcohol*. Hönig and Schubert¹ and Blonéau de Carolles² have described sulphuric acid esters of cellulose, soluble in water, which, when treated with alcohol, regenerate substances of the composition of cellulose, partly soluble, partly insoluble in water. When triturating cellulose with a small quantity of concentrated sulphuric acid in a glass mortar and adding to this a cold mixture of 3 parts concentrated sulphuric acid and 1 part concentrated nitric acid, we obtained nitrated products of snow-white color, soluble in alcohol, insoluble in ether and showing a nitrogen percentage varying with the temperature ruling during the action and the quantity of sulphuric acid. Even when trying to keep to the same conditions, the products varied from 10.22 to 11.29 per cent. nitrogen. By operating as follows we got up to much more highly nitrated products. About 2 grams of dry cellulose are completely dissolved in 50 cc. concentrated sulphuric acid and at once mixed with 25 or 30 cc. concentrated nitric acid, gradually run in from a drop funnel. The temperature should not rise over 15° which is secured by surrounding the vessel with ice. Now the mixture is allowed to stand at the ordinary temperature, which leads to the precipitation of a soft plastic mass. After twelve hours the whole is poured into a large quantity of water and this produces a precipitate of the following properties: It is a flocculent white powder, soluble in acetone, acetic ether, ethyl alcohol, methyl alcohol; it is precipitated by water from the alcoholic solution as a gelatinous mass and can be purified in this

¹ Monatsh. Chem., 6, 708, and 7, 455.

² J. prakt. Chem., [2], 32, 427.

manner. In concentrated nitric acid it dissolves with the greatest facility. Its nitrogen percentage is usually from 12.60 to 12.67, and it is therefore almost equal in nitrogen to decanitrocellulose; but occasionally we obtained as high as 13.80 per cent. nitrogen, and even this product was soluble in alcohol! We must probably look at these products as nitrated *cellulose-dextrines* or amyloids, and they must, of course, not be confounded with true nitrocelluloses.

Returning to the nitrocelluloses proper, as obtained in the usual way, we find that products soluble in ether-alcohol may be obtained almost down to the composition of heptanitrocellulose (10.19 per cent. nitrogen) and up to decanitrocellulose (12.78 per cent. nitrogen), or even beyond this. The collodion cotton of commerce, however, belongs more to the medium class of the composition of octonitrocellulose (11.13 per cent.) and enneanitrocellulose (11.98 per cent.). Where a high nitrogen percentage is not especially desired, but complete solubility is most important, it will be easiest to work for nitrogen percentages ranging from 11 to 11.5 per cent. by means of the acid mixtures indicated in Section III, C, Nos. 7 and 8, with nearly equal quantities of sulphuric and nitric acids, and from 19 to 20 per cent. water. These nitrocelluloses are insoluble in ordinary 95 per cent. alcohol, as well as in pure ether, but soluble in absolute alcohol. This might lead to the conclusion that in the ordinary ether-alcohol (3 : 1) the alcohol is the proper solvent. But this cannot be stated as a fact, for the solubility in absolute alcohol does not run parallel with that in ether-alcohol. The former rapidly decreases from 12 per cent. nitrogen upwards; at 12.04 per cent. nitrogen it is only 70 per cent.; the true decanitrocellulose which is perfectly soluble in ether-alcohol, yields only 1.3 per cent. to absolute alcohol.

A number of experiments were made to determine how far the mixture of ether (0.720) and alcohol (0.810) may be varied from the usual proportion 3 : 1. A nitrocellulose of 11.54 per cent. nitrogen dissolved easily in 6 ether to 1 alcohol; only 95 per cent. in 12 ether to 1 alcohol. In the last-mentioned case, 324 cc. ether to 26 cc. alcohol dissolved 1 gram nitrocellulose, which 26 cc. alcohol alone would not have done. A mixture of 27 ether to 1 alcohol dissolved only 7.3 per cent., on treating 1 gram with 350 cc.

In the other direction, 1/3 ether to 1 alcohol acted as a complete solvent; 1/6 ether to 1 alcohol dissolved only 93 per cent.;

but even with 1/5 ether to 1 alcohol the solubility was 95 per cent. This shows that the proportions of ether to alcohol may vary within very wide limits from the usual proportion of 3 : 1.

I append here the results obtained by examining various descriptions of *commercial collodion cotton*. This article, as everybody knows, is employed for extremely different purposes, and it seems likely from the outset that its properties, and hence, its composition and preparation should vary accordingly. For collodion cotton intended for surgical and photographic purposes, and for Chardonnet's vegetable silk, complete solubility in ether-alcohol is, no doubt, the most imperative requirement. When intended for blasting gelatine, that is, for forming a semisolid, tough mass with nitroglycerine, from 5 to 7 collodion cotton with 95 to 93 nitroglycerine, a high nitrogen percentage seems desirable together with solubility in nitroglycerine, which may not run parallel to that in ether-alcohol. Great secrecy is observed as to the manufacture of collodion cotton for both purposes, and even the composition of both is not sufficiently well known.

A sample of collodion cotton A, manufactured in Belgium expressly for blasting gelatine, showed 12.33 per cent. nitrogen and a solubility of 95.5 per cent. in ether-alcohol. Its explosion point, 198.5°, was almost exactly like that of collodion cotton B made for vegetable silk, 197°, and very little above that of guncotton. 13.25 per cent. nitrogen = 195°. The time of heating until explosion occurred, varied only from 4' 4" to 4' 48". The Abel test (Section III, H), in the case of guncotton occurred after 15' to 17'; in that of collodion cotton B after 20' to 24'. Cotton A did not give any result even after several hours, evidently owing to some admixture preventing the coloration of the test-paper.

We might infer from the above that collodion cotton, intended for the manufacture of blasting gelatine, should contain more nitrogen than that which is intended for dissolving in ether-alcohol. It should be prepared, according to our previous statement, with acid mixtures containing about 18.5 per cent. water.

I conclude this section with a few words on a paper by Kisniemsky¹ who has derived from Bruley's experiments a formula for calculating the nitrating mixtures leading to products of definite nitrogen percentages and definite solubilities. Taking

¹ *Mém. des poudres et saupètes*, 10, 64.

2 molecules HNO_3 as unity ($= 1$), and denoting 1 mol. H_2SO_4 by a , 1 mol. H_2O by c , he calls the magnitude $(1 + a) - c =$ the "characteristic" of the mixture. He asserts that mixtures with $\mu > 0$ yield products with much nitrogen and low solubility, mixtures with $\mu < 0$, soluble products, of which those where μ is only a like above — 1, contain the maximum of nitrogen.

It was not likely from the outset that the incomplete materials of which Kisniemsky disposed would lead to a mathematical formulation of the chemical action in question, an ambition which I do not even entertain for the much more complete materials offered in this paper. It may suffice to state that the indications yielded by his formula are quite uncertain and in many cases of the greatest importance they would be directly misleading. At all events they are useless for practical work.

H. Influence of the Lower Oxides of Nitrogen in the Acid Mixture on the Stability of the Nitrocelluloses.

Every description of commercial nitric acid, at least of higher strength, contains lower oxides of nitrogen. It is now generally assumed that in concentrated nitric acid (and we here deal only with such) the lower oxides consist essentially, if not exclusively, of nitrogen tetroxide, N_2O_4 , formerly called "hyponitric acid," and generally considered as the mixed anhydride of nitrous and nitric acid, $\text{NO}-\text{O}-\text{NO}_2$. This view is, of course, greatly complicated by the fact that the vapor of nitrogen tetroxide begins to split up, when heated above its boiling-point, into molecules of NO_2 , until at about 160° only such exist. But we need not go into a theoretical discussion of the behavior and constitution of this vapor, since we have here to deal merely with liquid N_2O_4 , and this certainly behaves entirely as a mixed anhydride in presence of strong sulphuric acid, the reaction being $\text{H}_2\text{SO}_4 + \text{N}_2\text{O}_4 = \text{NO}_2\text{H} + \text{SO}_2(\text{OH})(\text{ONO})$; that is, nitrogen tetroxide then splits up into equal molecules of nitric acid and nitrososulphuric acid (chamber crystals).

Surely the above reaction is a reversible one, and therefore we must assume the presence of some N_2O_4 in any mixture of sulphuric acid, nitric acid, and nitrososulphuric acid; but the exhaustive investigation of this subject by Lunge and Weintraub¹ has shown that the amount of free N_2O_4 is extremely small, if

¹ *Ztschr. angew. Chem.*, 1899, pp. 393 and 417.

there are equal quantities of sulphuric and nitric acids present, and is reduced to mere traces where the sulphuric acid prevails.

Since in the manufacture of nitrocelluloses we have always to deal with a mixture of strong sulphuric and nitric acids, we must assume that any nitrogen tetroxide introduced by the latter is converted in the acid mixture half into nitric acid and half into nitrososulphuric acid. As nitrososulphuric acid is a derivative of nitrous acid and easily regenerates the latter in contact with water, alkalies, etc., it is *prima facie* not impossible that it might form nitrous esters with cellulose; and even mere traces of free N_2O_4 might lead to the same result, since, on being destroyed by esterification, they would be re-formed from the mixture of nitric and nitrososulphuric acids. Now the nitrous esters of cellulose might tend more to spontaneous decomposition than the nitric esters, and this would diminish the stability of nitrocellulose. All this, however, is entirely hypothetical, and only actual experiment can show whether the presence of N_2O_4 in the original nitric acid does or does not affect the properties of the guncotton manufactured from its mixture with sulphuric acid.

Berthelot¹, when saponifying nitroglycerine, found a considerable proportion of potassium nitrite along with nitrate. But even if we apply this observation to guncotton, which would be quite arbitrary, it affords no proof of the quantity of nitrous esters originally present (not formed by secondary reactions) and still less of their action concerning the stability of the guncotton.

Practical manufacturers mostly consider the presence of "low oxides" injurious in the manufacture of both nitroglycerine and guncotton.² But I can find no proof whatever for this opinion, except a paper of Payen's, from the earliest childhood of nitrocellulose.³ He states that "hyponitric acid" diminishes both the yield and the nitrogen percentage of guncotton, and the guncotton thus produced also yielded inferior results with the ballistic pendulum, but there is nothing said about stability. Even if it were otherwise we could not acknowledge that ancient preparation of Payen's as a fair sample of guncotton and as a real proof for the action of N_2O_4 .

Apart from the question of stability, I have found Payen's

¹ *Compt. rend.*, September 17, 1900.

² Compare, for instance, the discussion in the New York Section of the Society of Chemical Industry, *J. Soc. Chem. Ind.*, 1900, p. 645.

³ *Compt. rend.*, 24, 86, 1847.

assertion concerning the nitrogen percentage and yield to be erroneous. In 1898 we made comparative tests, adding to a mixture of 3 parts concentrated sulphuric and 1 part concentrated nitric acid, various quantities (*viz.*, 2.10, 6.43, 12.01 per cent. liquid nitrogen tetroxide) but with the first two mixtures we found exactly the same percentage and yield, and only when adding 12.01 per cent. N_2O_4 , the nitrogen fell to 13.22 per cent., still quite a respectable figure. In 1900 we repeated this test, employing a mixture of 60.71 per cent. sulphuric acid, 30.67 per cent. nitric acid, 8.52 per cent. water, to which were added (as shown by analysis) various percentages of nitrogen tetroxide with the following results :

No.	N_2O_4 Per cent.	Nitrogen in guncotton, Per cent.	Yield. Per cent.
1	0.13	13.55	174.53
2	0.99	13.50	175.02
3	1.84	13.56	173.98
4	5.15	13.56	175.60

This proves that contrary to Payen's assertions and the opinion of many practical men *the presence of "low oxides" far above the proportion ever found in commercial acids has no influence whatever either on the nitrogen percentage or the yield of guncotton.*

This, of course, does not touch the question of stability. Before entering upon this, we had to ascertain which of the various methods for testing the stability of nitrocellulose was both trustworthy and applicable to our case. All these methods are empirical and to a great extent arbitrary, for they assume that the stability during a long period of ordinary (summer) temperatures, runs parallel with the evolution of nitrogen oxides during a short time of heating to higher temperatures. This may not, in reality, be the case, but I could not, of course, go behind the ordinary assumption, and it was merely the question of ascertaining which method it would be best to choose among those employed or proposed for testing commercial guncotton.

The oldest and even now most generally employed method is Abel's heat test, which is too well known to need description here. The principal objection to it is that it fails in the presence of mercuric chloride and perhaps of other substances added to commercial guncotton for the purpose of preventing mildew, but this of course could not interfere with our experiments, where no such ingredients come into play.

Principally on account of the just-mentioned drawback Guttmann proposed diphenylamine as an indicator, to be employed just like the potassium iodide in the Abel test, by observing a blue streak suddenly appearing between the wet and dry portion of the test paper.¹ Thomas² and Spica³ reject Guttmann's test; but although we could certainly not notice the *sudden* appearance of the blue streak as described, we succeeded, after some practice, in obtaining sufficiently concordant results by means of that test as will appear below.

Spica himself recommends metaphenylenediamine which we had no opportunity of testing, as his communication reached me after the conclusion of that part of our work; it is probable that this reagent would be *too* delicate for practical purposes.

Thomas indeed rejects all test papers as being too sensitive, and applies a pure heat test, consisting in heating the samples during eight or ten hours at 100° until red vapors appear.

A most interesting discussion on stability tests in the London Section of the Society of Chemical Industry⁴ and the above-mentioned highly important paper by Professor W. Will, printed for private circulation by the New Babelsberg Central Station for scientific technical investigations in December, 1900, were equally too late for the purposes of my own investigation, but they would not have affected it to a great extent. It is, however, very important to notice that Will comes to the conclusion that the results obtained by the Abel test (which was employed in reaching my conclusions) are mostly in satisfactory agreement with those obtained by his own test; *viz.*, estimating the quantity of nitrogen given off by nitrocellulose when being heated to 135° during four hours. This test he considers to be much more indicative of the stability of such products than all tests founded upon the first appearance of nitrous vapors as utilized in all other tests. I believe therefore we have a right to say that the conclusions drawn from the following experiments are based on a trustworthy foundation.

To compare the stability of samples of guncotton prepared with or without "low oxides" of nitrogen, we had first to try how

¹ *J. Soc. Chem. Ind.*, 1897, pp. 288, 293; *Ztschr. angew. Chem.*, 1897, pp. 233 and 265; 1898, p. 1103.

² *Ibid.*, 1898, p. 1027.

³ *Moniteur Scientifique*, 1900, p. 313.

⁴ *J. Soc. Chem. Ind.*, 1901, p. 8.

far the methods employed for washing the product affected the heat tests. A properly nitrated sample was washed for three days with cold water, renewed every hour, always removing the previous water by a vacuum filter ; the washing was continued for three days with hot water of about 90° in the same way. Half of this sample (A) was dried in a current of dry air at 40°, the other half (B) in a vacuum desiccator over sulphuric acid. The first (A) stood the Abel test at 70° for 4'15", the second (B) for 2'1"—both quite insufficiently. Since Thomas had asserted that his test sometimes yields results entirely opposite to the Abel test, we subjected another sample of the same product to his test, by means of an oil-bath provided with a thermoregulator, but half a minute after the thermometer had marked 92°, a violent explosion occurred, shattering the whole apparatus, and we cannot therefore, in the interest of the safety of the manipulator, recommend the application of Thomas' tests to samples showing a very low Abel test. Where the Abel test yielded a good result, we applied Thomas' test without any accidents.

No better results were obtained by washing during seven days, partly cold, partly hot, with mechanical agitation of the guncotton in the bath. When adding to this treatment another day's washing with hot water, to which a little sodium carbonate was added, so that alkaline reaction existed up to the end, and assuredly no free acid could be left in the fiber, the Abel test went up only to 8', still quite an insufficient result.

Clearly the cause of this could not be any free acid still present in the guncotton ; one must think of unstable products formed by the action of the acids on foreign substances present in the cellulose or from cellulose itself by secondary action. Will and Lenze¹ have examined many nitrated carbohydrates (which might be thought of in this respect) for their stability, and found them generally very unstable ; some of these, even when previously insoluble in water, would be removed by boiling with water for some time, which is an operation always carried out in manufacturing guncotton on the large scale.

Lenk and Cross² remove such foreign substances by means of acetone, diluted with water to such an extent that it does not dissolve the guncotton itself, and they thus obtain an Abel test up

¹ *Ber. d. chem. Ges.*, 1898, p. 68.

² *J. Soc. Chem. Ind.*, 1900, p. 642.

to fifty-five minutes. This is no doubt correct but we succeeded quite as well in reaching that limit without the above treatment by merely boiling with water during three days.

We therefore proceeded in all further experiments as follows : After washing out most of the acid with cold water, the guncotton was cut into minute fragments (to imitate the action of the pulping engine) and boiled for several days with frequently renewed water, and we thus attained a sufficient degree of stability. It is unnecessary to say that we had started with highly purified cotton wool, and no fatty matters or other accidental impurities could influence the stability of the product.

The following comparative tests were made with this guncotton.

No.	Temperature of test.	Abel test.	Guttmann test.	Thomas test.
1	66°	17'-15'	24'-23'	3 to 2½ days.
2	70°	13'-14'	19.5'-20'	
3	80°	6'-6'	10'-12'	

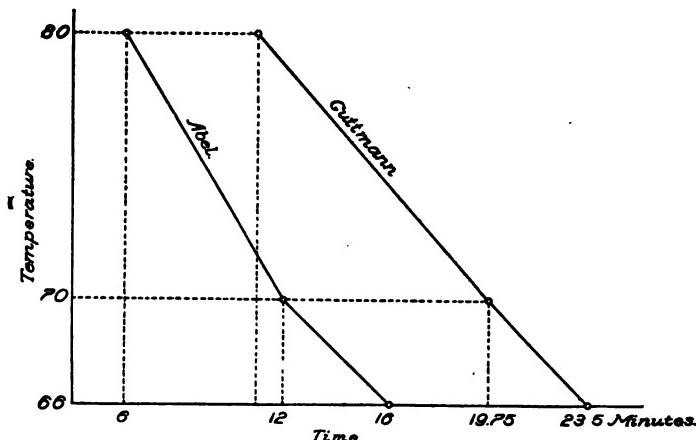


Diagram 3.

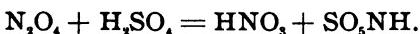
The tests No. 1, 2, and 3 were made at different times ; when made simultaneously, the tests agreed even better than the above. There is a distinct parallelism between Abel's and Guttmann's tests, although the absolute values are naturally different, owing to the difference in the sensitiveness of the reagents. This parallelism comes out very well in the graphical delineation of the results as shown here.

Evidently we might have employed either Abel's or Guttmann's

test for our purpose, as we had nothing to do with the ingredients masking the former ; and as the final point is rather better marked in the former than in the latter, we adhered to Abel's test.

In order to apply it to the question to be decided, a number of precisely parallel experiments was made, with the only difference that in each case one nitration was made in the absence of nitrogen tetroxide, the other in the presence of certain quantities of such. The acid mixtures were always the same ; the operation was carried out at the same time, the products being washed and dried precisely in the same way and tested in the same water-bath. Unless such absolute parallelism is kept up, the results may vary and may be deceptive, as proved by a number of preliminary experiments.

Series I.—The nitrating mixture consisted of 3 parts sulphuric acid (sp. gr. 1.84), and 1 part nitric acid (sp. gr. 1.52). Half of it was mixed with 4.93 per cent. nitrogen tetroxide, estimated by titrating the mixture with potassium permanganate, and a sufficient quantity of pure nitric acid was added to the other half to represent the HNO₃ formed from N₂O₄, according to the reaction :



The products obtained by nitrating cellulose with both mixtures at the same time, were freed from acid by pressing, cold washing, cutting up most finely, boiling with frequently renewed water for four days, pressing and drying for six days in a vacuum desiccator. Each time a sample of known quality (kept in the damp state and dried immediately before the experiment) was tested along with the other samples in order to make sure of the unchanged sensibility of the test-paper. Usually the time and temperature of explosion was also ascertained by heating 0.01 gram in a test-tube in an oil-bath. The samples left over from testing were taken out of the test-tube, spread on large watch-glasses protected against dust, and the test repeated after some time.

For each test 1.2 grams dry guncotton were weighed out and each sample tested in duplicate, all four being heated at the same time in the same water-bath.

RESULTS.

Date of test.	Without nitrogen tetroxide.		With nitrogen tetroxide.		Check sample for controlling the test-paper.
	a' 25'	a'' 27'	b' 37'	b'' 36'	c 14
Dec. 5, 1899.	{ Expl. 188.5° Time 5'11"		{ 188° 5'10"		{ 195° 6'
Jan. 12, 1900.	44'	45'	52'	50'	13'
	{ Expl. 187° Time 5'35"		{ 186° 5'33"	{ 201° 4'30"	
March 6, 1900.	55' { Expl. 187° Time 5'30"	54'	64' { 186.5° 5'29"	64'	{ 196° 6'

The first line always shows the time required for the Abel test at 80°; the second the explosion temperature; the third the time elapsing before an explosion occurs.

The Thomas test showed for samples *a*, two and one-half days; for samples *b*, three days; for samples *c*, three days.

The result was that in each case the guncotton prepared with nitrogen peroxide showed a distinctly better Abel test than that prepared without nitrogen tetroxide. Of course, I am far from generalizing this, but I am bound to state the fact as found. The explosion of the first kind of guncotton (samples *b*) certainly took place a few seconds before samples *a*, and at 0.5° or 1° lower temperature, but this does not appear to be an appreciable difference. The second explosion could not have been brought about by the first, for the samples *c* throughout maintain their distance from *a* and *b*, although heated in the same oil-bath. It should be noted that there is no parallelism between the Abel test and the explosion test; the samples *c*, strongly inferior as to the former, required a considerably higher temperature for explosion.

The fact that the repetition of the test after an interval of one or two months always yielded higher results, may possibly be explained by the slight loss of nitrogen during the testing. However, it is remarkable that the stability was not diminished, but considerably raised, by repeatedly heating to 80°.

The Thomas test also came out better for the guncotton prepared with nitrogen tetroxide than for the other kind.

Series II.—The addition of nitrogen tetroxide was now raised to 9.28 per cent. In this case we wished to determine also the yield, for which purpose the mass, each time when the water was

to be removed, was poured through a paper filter attached to a vacuum pump, while in Series I, where porcelain funnels with sieve-plates and filter-pumps were employed, the guncotton remained perfectly white; in Series II, a small quantity of brown matter collected at the bottom of the filter, and in the Abel test the test-paper was deeply stained after three minutes. This bad result could be referred only to the brown matter just mentioned. This was removed by repeating the boiling several times, and this time again passing the mass through a porcelain sieve, which allowed the brown substance to pass through, together with a few fibers of guncotton, both settling out from the filtrate. The quantity of the brown matter was too small for detailed investigation; it decomposed at 193°, with carbonization, but without explosion; it was insoluble in dilute acetone, and hence not identical with the substance to which Lenk and Cross attribute the instability of guncotton. This brown matter appeared in both cases, *a* and *b*, and has consequently nothing to do with the nitrogen tetroxide. It was probably formed by local overheating of fibers carried to the upper part of the flask during the boiling. The guncotton after the last described treatment was perfectly white and of sufficient stability.

This time the tests were carried through twice over (A and B) at different times, each time with two samples, exactly as in Series I, the water-bath being kept at 80°.

A.

Date of test.	Samples without N ₂ O ₄ .		Samples with N ₂ O ₄ .		Check sample for paper <i>c.</i>
	<i>a'</i> .	<i>a''</i> .	<i>b'</i> .	<i>b''</i> .	
Jan. 7, 1900.	15'	14'	17'	18'	15'
	{ Expl. 186.5°		{ 186°		{ 199°
	Time 4' 1"		4'		5' 40"
Jan. 26, 1900.	37'	40'	41'	47'	15'
	{ Expl. 1.86°		{ 185.5°		
	Time 4' 42"		4' 40"		
March 13, 1900.	48'	47'	45'	51'	14'
	{ Expl. 190°		{ 188°		
	Time 3' 36"		3' 34"		

B.

Date of test.	Samples without N ₂ O ₄ .		Samples with N ₂ O ₄ .		Check sample for paper <i>c.</i>
	<i>a'</i> .	<i>a''</i> .	<i>b'</i> .	<i>b''</i> .	
Jan. 5, 1900.	15'	13'	15'	12'	16'
	{ Expl. 186.5°		{ 186°		{ 201°
	Time 4' 26"		4' 25"		4' 20"

Date of test.	Samples without N ₂ O ₄ .		Samples with N ₂ O ₄ .		Check sample for paper. <i>c.</i>
	<i>a'</i>	<i>a''</i>	<i>b'</i>	<i>b''</i>	
Feb. 3, 1900.	36'	34'	34'	35'	15
	{ Expl. 186.5°		{ 185.5°		
	Time 5' 2"		5'		
March 13, 1900.	47'	49'	51'	56'	15
	{ Expl. 191°		{ 190.5°		:
	Time 3' 5"		3' 4"		

Both Series II, A, and II, B, agree with the results of Series I in showing that the presence of nitrogen tetroxide does not lower the Abel test, in the raising of the test on repetition, and in the minute difference of the explosion temperatures. It is also interesting to note that the results of Series II, A and B, although carried out at different times, agree excellently with each other.

The nitrogen percentage of sample *a* was 13.04, of sample *b* 13.09, both practically the same, but somewhat lower than the acid mixture employed would have yielded without the prolonged boiling; *viz.*, 13.35 to 13.42. Guttmann¹ notices this lowering of the nitrogen percentage by boiling on the large scale, while Bruley,² after 260 hours' boiling, found a diminution of only 1 cc. NO = 0.06 per cent. nitrogen.

Series III.—Since in the last series we had not handled gun-cotton of the highest percentage, owing to the three days' boiling, we prepared a new sample with only one day's cold washing and four hours' boiling. It showed 13.37 to 13.35 per cent. nitrogen, which is quite equal to a good commercial guncotton. The stability test yielded.

Date of test.	Without N ₂ O ₄ .	With N ₂ O ₄ .
June 21, 1900.	3' - 3' 20"	3' - 3' 40"
July 4, 1900.	4' - 4' 15"	4' - 4' 19"
	{ Expl. 166°	164°
	{ Time 3' 52"	3' 50"

The stability is low, but again there is no difference in favor of the product made without nitrogen tetroxide.

Ultimately we tested for solubility, because Payen had asserted that the guncotton made in the presence of nitrogen tetroxide is soluble in ether-alcohol; that made without nitrogen tetroxide insoluble. We found absolutely no difference in this respect, and Payen's statements of the year 1847 must therefore be altogether excluded from further consideration.

¹ "Schiss und Sprengmittel," p. 86.

² *Mém. des poudres et salpêtres*, 8, 131.

The above shows that nitrogen tetroxide, when added to a mixture of strong sulphuric and nitric acids, even up to the enormous amount of 9.28 per cent., has no such deteriorating action on the stability of guncotton as is generally assumed. But for the sake of completeness it may be mentioned that free nitrogen tetroxide, in the liquid form, has a destructive action on cellulose. 100 grams liquid nitrogen tetroxide, acting on 8 grams pure cotton during three days in the ice-safe, converted it into a viscid mass, the fibers being strongly enlarged, and mostly soluble in boiling water. The solution reduces Fehling's solution on boiling and gives precipitates with phenylhydrazine (insoluble in the ordinary organic solvents) as well as with lead, silver, and barium salts.

I believe this fully justifies the conclusion that *nitrogen tetroxide ("low oxides") in the nitric acid, even far beyond the proportion ever found in commercial acids, has no injurious action in the manufacture of guncotton, neither toward nitrogen percentage, yield, nor stability as measured by the ordinary tests.* I should have liked very much to approach the same question for *nitroglycerine*, which may or may not behave in a way similar to nitrocellulose; since the prejudice against nitrogen tetroxide has proved to be wrong in one case, it might possibly be so in the other case. But I must leave this task to others; the handling of *nitroglycerine* is so much more dangerous than that of nitrocellulose that I did not feel justified in undertaking such work in a public laboratory where hundreds of students congregate.

I. Behavior of Different Commercial Grades of Cotton in Nitration, Especially for the Manufacture of Collodion Cotton.

All our researches had been made with the same material, *viz.*, the purest form of cellulose obtainable in the shape of "surgical cotton wool," which is, of course, much too expensive for manufacturing commercial nitrocelluloses.

In ordinary practice good cotton waste, mechanically purified, and boiled in alkaline solutions, is the material of the manufacturer. Of course this cotton waste belongs to many different commercial grades of cotton, and some practical men believe that their failure to obtain uniform products is caused by differences in the original cotton. Especially it is believed that this accounts for the alleged "fact" that by the same mixture of acids (?)

sometimes a soluble, sometimes a difficultly soluble, collodion cotton is obtained.

Looking at the complicated structure of the cellulose molecule on the one side, and at the greatly varying morphological structure of the vegetable fiber, even that of various species of cotton fiber, on the other side, it cannot be denied that there is some *prima facie* reason for the above assumption.

Nettlefold¹ obtained different products when nitrating wood fiber and cotton by the same acid mixture ; the former yielded a product with 11.2 per cent. nitrogen, and 41.6 per cent. soluble matter ; the latter yielded the highest degree of nitration and only 8 per cent. soluble matter. I am not aware whether wood fiber ("cellulose" of the German manufacturer, made by various processes, *viz.*, the soda, sulphate, and sulphite processes) is anywhere used in the manufacture of collodion cotton, but even when confining ourselves to ordinary cotton, there might have been something in the opinion that various grades of this would behave differently in the nitrating process. Indeed I must confess that I started from this as the most probable assumption.

In order to bring it to a test, I procured from the leading cotton mills in Switzerland authentic samples of the most varying grades of cotton, which were carefully cleaned mechanically and washed in the same way as in the manufacture of guncotton and nitrated with the same acid mixture (63.84 sulphuric, 16.96 nitric acid, 19.20 water), keeping all the conditions of the experiments exactly alike. Together with these we nitrated a sample of our "chemically pure surgical cotton wool," with the following results :

No.	Commercial designation.	Solubility in		
		Nitrogen. Per cent.	ether-alcohol. Per cent.	Yield. Per cent.
1.	Chemically pure surgical cotton wool	11.76	100	159
2.	American cotton " middling fair " . . .	11.56	100	157
3.	American cotton " Florida "	11.67	100	153
4.	Egyptian cotton, white, " Abassi " ..	11.69	100	155
5.	Egyptian cotton, natural yellow.....	11.61	100	154

This shows that, contrary to my own assumption, *there is no essential difference in the quality of the collodion cotton obtained from these extremely differing grades of cotton.* They are all completely soluble; the nitrogen differs only by 0.13 per cent. among all the commercial cottons, and only by 0.20 *in maximo* against

¹ *Chem. News*, 55, 306.

the pure surgical cotton. The latter is easily explained by the difference in purity, the surgical cottons containing only 0.05 per cent. ash, the commercial cottons averaging 0.5 per cent. ash, but this is evidently quite immaterial for manufacturing purposes.

The varying results observed in manufacturing nitrocellulose, especially collodion cotton, must therefore *not* be attributed to variation in the quality of the cotton employed, but most probably to unequal conditions of nitration, perhaps as regards temperature, but most probably as regards differences in the percentages of water contained in the acid mixture, which may have been overlooked by the manufacturer. The preceding investigation shows that even very slight differences in the percentage of water may be of the greatest importance for the result, more important than even much greater differences in all other respects.

ZURICH, May, 1901.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
No. 57.]

THE ELECTROLYTIC SEPARATION OF MERCURY FROM COPPER.

BY C. ROSCOE SPARKE AND EDGAR F. SMITH.

Received June 25, 1901.

A T intervals, since the electrolytic separation of mercury from copper was first announced, statements have appeared that the separation was unsatisfactory. The first objection was to the length of time consumed, but it was soon observed in this laboratory that this factor was very materially reduced upon heating the electrolyte to 65° C. Then it was said that the separation was only applicable and satisfactory when the quantity of copper was not too large, as compared with the amount of mercury in the solution. Proper replies were made to these restrictions upon the method, but recently another chemist, in the person of Emil Goecke, published in his inaugural thesis "Ueber den Genauigkeitsgrad elektro-analytischer Arbeitsmethoden," etc., that he not only required from sixteen to twenty-four hours to effect the separation, but that in only three instances did he find the mercury free from copper. It is not the purpose of the writers to question Goecke's ability to conduct electrolytic work, or analytical work of any kind for that matter, but they feel that it is only fair to lay additional actual experience before the reader, leaving time and further trials to determine finally who is right.

In this laboratory the method in question has been so frequently carried out with success that it seemed almost useless to repeat; but the following trials were undertaken and the results are presented in the order in which they were obtained. The details are sufficiently indicated in the tables.

TABLE.
In the approximate proportion of 1 Hg : 1 Cu.

Mercury. Gram.	Copper. Gram.	KCN. Gram.	Dilution. cc.	Current.	voltage.	Temperature. °C.	Time. Hours.	Mercury found. Gram.
0.1211	0.1520	2.5	125	N.D. ₁₂₅ = 0.03 A	{ 1.2 V 1.7 V	65°	3 $\frac{1}{4}$	0.1211
0.1211	0.1520	2.5	125	N.D. ₁₂₅ = 0.05 0.03 } ¹	{ 1.2 V 1.9 V	60°	2 $\frac{1}{2}$	0.1208
0.1211	0.1520	2.5	125	N.D. ₁₂₅ = 0.03 0.015 }	{ 1.2 V 1.5 V	63°	3 $\frac{1}{4}$	0.1211
1 Hg : 2 $\frac{1}{2}$ Cu.								
0.1211	0.3040	3.5	125	N.D. ₁₂₅ = 0.03 0.015 }	{ 1.2 V 1.5 V	65°	3 $\frac{1}{2}$	0.1202
0.1211	0.3040	3.5	125	N.D. ₁₂₅ = 0.03 0.02 }	{ 1.2 V 1.5 V	65°	3 $\frac{1}{2}$	0.1205
0.1211	0.3040	3.5	125	N.D. ₁₂₅ = 0.03 0.02 }	{ 1.2 V 1.5 V	65°	4	0.1210
1 Hg : 6 $\frac{1}{2}$ Cu.								
0.0453	0.3040	3.5	125	N.D. ₁₂₅ = 0.03 0.012 }	{ 1.1 V 1.5 V	65°	2 $\frac{1}{2}$	0.0453
0.0453	0.3040	3.5	125	N.D. ₁₂₅ = 0.03 0.02 }	{ 1.2 V 1.5 V	65°	3	0.0455
0.0453	0.3040	3.0	125	N.D. ₁₂₅ = 0.03 0.01 }	{ 1.1 V 1.5 V	60°	4 $\frac{1}{4}$	0.0449
1 Hg : 11 Cu.								
0.0453	0.5115	6.0	135	N.D. ₁₂₅ = 0.03 0.015 }	{ 1.2 V 1.5 V	65°	2 $\frac{1}{2}$	0.0453
0.0453	0.5115	7.5	135	N.D. ₁₂₅ = 0.03 0.015 }	{ 1.1 V 1.5 V	60°	3 $\frac{1}{2}$	0.0447
0.0453	0.5115	5.5	135	N.D. ₁₂₅ = 0.03 0.01 }	{ 1.2 V 1.5 V	60°	2 $\frac{1}{2}$	0.0454
3 Hg : 1 Cu.								
0.1211	0.0483	2.5	125	N.D. ₁₂₅ = 0.022 0.02 }	{ 1.5 V 1.5 V	60°	2 $\frac{1}{4}$	0.1210
0.1211	0.0483	2.3	125	N.D. ₁₂₅ = 0.03 0.01 }	{ 1.5 V 1.5 V	60°	4 $\frac{1}{4}$	0.1213
0.1211	0.0483	2.0	125	N.D. ₁₂₅ = 0.06 0.01 }	{ 1.6 V 1.5 V	65°	3	0.1205

¹ Maximum and minimum currents.

The deposit of mercury was, in each case, tested most carefully for copper, but the latter was never found. Why Goecke encountered the opposite experience we are not prepared to say. The only reagent used for washing was cold distilled water. The source of the electric energy was storage cells. The time factor here, as in numerous other experiments, is much reduced. From the abundance of evidence here presented on this topic and in former communications we are disposed to leave the controversy to those who delight in such occupation. We submit facts. They alone settle difficulties.

Goecke emphasizes the statement that carbon is present in metals deposited by the current from potassium cyanide solutions, "jedoch in so minimalen Mengen, dass dieselben für die Praxis kaum in Betracht kommen." Indeed, in but a single instance did it attain to 0.1 per cent., so that another writer has said "aber in so minimaler Menge, dass die Versuchsfehler der Bestimmungsmethoden kaum überschritten wurden." And we are disposed to add that in all probability a more thorough washing of the precipitated mercury would have removed the last traces of alkaline cyanide and the test for carbon would have resulted negatively.

One of the chief purposes of Goecke seems to have been the study of the impurities contained in metals precipitated on the cathode. He points to the occurrence of carbon in the iron deposited from a citrate solution. This fact was commented upon by the person who first precipitated iron from that electrolyte. It is an old story, and before long we shall very probably hear from Dr. E. F. Kern on this subject. He has executed a series of experiments showing upon what this co-precipitation of carbon is due and how it may be avoided. In time, too, we hope to speak of the occurrence of phosphorus in metals, deposited from solutions of phosphates. Goecke records it as an ever-present impurity in the metals deposited from such electrolytes.

But to return to the electro-deposition of mercury. The literature relating to this reveals the fact that very little experimentation in this way has been done with mercury in the presence of three or four other metals. Indeed, this is a direction in which investigation could be profitably conducted. We submit results obtained by us in following this thought.

Mercury. Gram.	Copper. Gram.	Cadmium. Gram.	KCN. Grams.	Dilution. cc.	Current.	Voltage.	Temperature. °C.	Time. Hours.	Mercury found. Gram.
0.12II	0.1207	0.1410	4.0	135	N.D. ₁₂₅ = 0.04 A } { 0.01 A }	{ 1.4 V 1.5 V	65°	3½	0.1204
0.12II	0.1207	0.1410	3.5	135	N.D. ₁₂₅ = 0.04 A } { 0.01 A }	{ 1.2 V 1.5 V	65°	3½	0.12II
0.12II	0.1207	0.1410	3.0	135	N.D. ₁₂₅ = 0.02 A } { 0.01 A }	{ 1.4 V 1.5 V	65°	4	0.1207
0.12II	0.1207	0.1410	3.0	135	N.D. ₁₂₅ = 0.03 A } { 0.01 A }	{ 1.3 V 1.5 V	60°	4½	0.1203
0.12II	0.1207	0.1410	3.0	135	N.D. ₁₂₅ = 0.04 A } { 0.01 A }	{ 1.4 V 1.5 V	60°	4	0.1208

Mercury. Gram.	Copper. Gram.	Cadmium. Gram.	Zinc. Gram.	KCN. Grams.	Dilution. cc.	Current.	Voltage.	Temperature. °C.	Time. Hours.	Mercury found. Gram.
0.12II	0.1207	0.1410	0.1000	9.0	135	N.D. ₁₂₅ = 0.02 A } { 0.01 A }	{ 1.4 V 1.5 V	60°	5	0.1206
0.12II	0.1207	0.1410	0.1000	5.0	135	N.D. ₁₂₅ = 0.03 A } { 0.01 A }	{ 1.5 V 1.5 V	60°	3½	0.1207

UNIVERSITY OF PENNSYLVANIA.

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THE PRECIPITATION AND SEPARATION OF SILVER IN THE ELECTROLYTIC WAY.

By W. H. FULWEILER AND EDGAR F. SMITH.

Received June 25, 1901.

THE fact that silver can be quantitatively determined in the electrolytic way is well known. It has had ample confirmation in this laboratory, where numerous estimations of the metal in cyanide solution have been made. It is probable, too, that it was here that the first quantitative results with this electrolyte were obtained although it is customary to credit the method to Luckow notwithstanding, in his published account of the electro-deposition of silver from its double cyanide solution, he presents no quantitative data, and merely remarks in regard to such solutions: "So fällt aus solchen Lösungen das Silber gleichmässig in regulinischer form mit mattem Metallglanze nieder."¹ But be that as it may, without any further reference to the origin of the method, the latter is most deserving of consideration, and to

¹ *Ztschr. anal. Chem.*, 19, 15.

extend in some measure its general applicability we have made separations of silver from solutions in which three or four other metals were simultaneously present. It is the results in this direction which we most desire to put upon record.

Those interested in electrochemistry will at once recall that in the hundreds of separations made with the current more than two metals rarely were present in the electrolyte. Now that electrochemical analysis is daily becoming more prominent the proper working conditions for such problems should be ascertained. It is probable that this phase in electrolysis has been too long neglected. We give first results obtained with silver alone.

Silver. Gram.	Dilu- tion. cc.	Potassium cyanide. Grams.	Current. N.D.100-	Volts.	Temper- ature. 65°	Time. Hours.	Silver found. Gram.
1	0.2133	125	2	0.03 A	2.5	65°	4
2	0.2133	125	2	0.03 A	2.5	60°	3
3	0.2133	125	4	0.04 A	2.5	60°	3
4	0.2133	125	2	0.025 A	2.7	60°	4
5	0.2133	125	2	0.025 A	2.7	60°	3
6	0.2133	125	2	0.025 A	2.7	60°	4

In trials 1 and 2 the metal was precipitated upon a dish, while in 3 and 4 a plate cathode, and in 5 and 6 a cone was used to receive the silver, which was very adherent, and brilliant in luster. It was washed with water, alcohol, and ether.

The first thought was to further test the separation of silver from copper, making a special point in varying the quantity of the latter metal.

SILVER FROM COPPER.

Silver. Gram.	Copper. Gram.	Potassium cyanide. Grams.	Dilu- tion. cc.	Current. N.D.100-	Volts.	Temper- ature. 60°	Time. Hours.	Silver found. Gram.
0.1066	0.1053	2	125	0.021 A	1.2	60°	4½	0.1066
0.1066	0.1053	2	125	0.02 A	1.25	55°	6	0.1064
0.1066	0.1053	2	125	0.02 A	1.25	55°	6	0.1065

The silver was completely precipitated. It was found to be free from copper.

The next ratio was 1Ag : 2Cu :

Silver. Gram.	Copper. Gram.	Potassium cyanide. Grams.	Dilu- tion. cc.	Current. N.D.100-	Volts.	Temper- ature. 60°	Time. Hours.	Silver found. Gram.
0.1066	0.2106	2	125	0.02 A	1.25	60°	3½	0.1066
0.1066	0.2106	2	125	0.02 A	1.25	65°	3½	0.1065

With the ratio 1Ag : 5Cu the results were :

Silver. Gram.	Copper. Gram.	Potassium cyanide. Grams.	Dilu- tion. cc.	Current. N.D.100.	Volts.	Temper- ature. °	Time. Hours.	Silver. found. Gram.
0.1066	0.5265	4	125	0.03 A	1.2	65°	3½	0.1066
0.1066	0.5265	4	125	0.02 A	1.2	60°	3½	0.1068

The experience gathered from these determinations shows that the separation of these two metals can be conducted in this particular way with the certainty of success. In several instances the liquid from the silver was diluted to 500 cc. and electrolyzed with a more powerful current when the copper was fully precipitated and showed the absence of silver upon applying the customary tests.

SILVER FROM COPPER AND CADMIUM.

Silver. Gram.	Copper. Gram.	Cadmium. Gram.	Potassium cyanide. Grams.	Dilution. cc.	Current, N.D.100 in A.	Volts.	Temperature. °	Time. Hours.	Silver found. Gram.
0.1066	0.1053	0.1128	3	125	0.02	1.25	65°	3½	0.1063
0.1066	0.1053	0.1128	3	125	0.015	1.25	65°	4	0.1069
0.1090	0.1053	0.1128	3	125	0.02	1.25	65°	4	0.1090

The next step was the introduction of a zinc salt into the electrolyte. Strangely enough some cadmium was now found in the deposit of silver, but it was not long before the observation was made that if the electrolyte was heated to 75°–80° before passing the current the co-precipitation of cadmium could be absolutely prevented. The conditions are indicated in the subjoined table :

Silver present. Gram.	Copper present. Gram.	Cadmium pres- ent. Gram.	Zinc present. Gram.	Potassium cy- anide. Grams.	Dilution. cc.	Current. N.D.100.	Volts.	Temperature. °	Time. Hours.	Silver found. Gram.
0.1090	0.1053	0.1128	0.1244	4	125	0.02 A	1.25	80°	5	0.1092
0.1090	0.0526	0.0564	0.0622	5	125	0.02 A	1.25	75°	6	0.1089
0.1090	0.0526	0.0564	0.622	3.5	125	0.02 A	1.25	75°	5	0.1087

The silver was found free from any of the other metals. In all the experiments made with the conditions as recorded in the preceding paragraphs the striking, brilliant luster of the deposited silver was particularly marked.

SILVER FROM COPPER, CADMIUM, ZINC, AND NICKEL.

Silver. Gram.	Copper. Gram.	Cadmium. Gram.	Zinc. Gram.	Nickel. Gram.	Potassium cy- anide. Grams.	Dilution. cc.	Current. N.D.-100.	Volts.	Temperature. 75° C.	Time. Hours.	Silver Gram. found.
0.1090	0.0526	0.0564	0.0622	0.0411	4.5	125	0.02 A	1.2	75° C	5½	0.1086
0.1090	0.0526	0.0564	0.0622	0.0411	3.5	125	0.02 A	1.2	75° C	5	0.1085

None of the other metals were found in the silver deposit. The addition of the nickel to the solution seems to retard the precipitation of silver to a slight degree.

UNIVERSITY OF PENNSYLVANIA.

NOTES ON THE ANALYSIS OF EXPLOSIVES.

BY F. W. SMITH.

Received May 15, 1901.

DETERMINATION OF SULPHUR.

In gelatine dynamite containing from 1 to 3 per cent. of sulphur, the following method is useful: Weigh out about 2 grams into a silver crucible of 100 cc. capacity: fill it two-thirds full with an alcoholic solution of caustic soda. Warm carefully on a water-bath until the nitroglycerine is decomposed and then evaporate to dryness. Add next about 40 grams of solid caustic potash and 5 grams of potassium nitrate. Fuse the contents of the crucible carefully over a blast-lamp until all organic matter is oxidized. Dissolve in dilute acetic acid, filter from a small amount of insoluble matter, and precipitate the sulphates with the usual precautions. The results check very closely.

AN INDIRECT METHOD FOR THE ESTIMATION OF NITROGLYCERINE
IN GELATINE DYNAMITE, ETC.

About 15 grams of the sample are completely extracted with chloroform in a Soxhlet apparatus and the loss in weight noted. In another portion the moisture is determined by desiccation over sulphuric acid for five days, careful experiments having shown that nitroglycerine is not appreciably volatile in a desiccator. Another portion of about 2 grams is carefully extracted with pure ether by maceration in a small beaker. The ether is poured through a filter and the extraction repeated three or four times. The filtrate is now allowed to evaporate spontaneously or with the aid of a gentle current of air. When the

ether is evaporated add about 5 cc. of ammonium sulphide solution and 10 cc. of alcohol. Warm gently on a water-bath until the nitroglycerine is decomposed and then add about 250 cc. of water and enough hydrochloric acid to give a strongly acid reaction, filter, and wash the precipitate free from acid. Now wash the precipitate out with strong alcohol and chloroform, collecting this filtrate in a weighed platinum dish. Evaporate at a low temperature and dry to constant weight at 50° C. The contents of the dish are now transferred to a silver crucible and the sulphur determined as above described. The increase in weight of the dish less this amount of sulphur represents the chloroform-soluble substances in the original sample except the nitroglycerine, moisture, and sulphur. The percentage of the former substances plus the moisture and sulphur in the original sample gives, when subtracted from the total chloroform-soluble, the percentage of nitroglycerine.

In another portion, the residue in the platinum dish may be investigated for resins, paraffin, etc.

ON THE USE OF LUNGE'S NITROMETER.

All the glass stop-cocks should be tight. In reference to the practical testing of stop-cocks, see this Journal, 21, 430.

Standardizing the Nitrometer.—There are two methods applicable, the first of which I shall call the 'absolute method' and the second the 'empirical method.' The latter was devised by Dr. Clarence Quinan, of San Francisco.

The first consists in admitting to the reduction tube a quantity of air such that if reduced to 0° C. and 760 mm. pressure, it would occupy a volume of 100 cc. The analysis is then made by weighing out a convenient quantity of nitrate, decomposing it in the usual way, introducing the nitric oxide into the measuring tube and regulating the pressure, so as to bring the volume of air in the reduction tube to 100 cc., while the surface of the mercury in the measuring tube is at the same level as the surface of the mercury in the reduction tube. If deemed preferable the level of the mercury in the measuring tube may be made to coincide with the level of the mercury in the reservoir tube so as to make the pressure in the measuring tube equal to the atmospheric pressure. The volume of nitric oxide is then read off and reduced to normal conditions by the usual calculations.

The correctness of the results obtained in this method, aside from errors of manipulation, is affected by the following factors:

- (A) The accuracy of the barometer.
- (B) The accuracy of the thermometer.
- (C) The accuracy of the graduation of the reduction tube.
- (D) The accuracy of the graduation of the measuring tube.
- (E) The accuracy of the weights employed.

It is evident that the work of calibrating all the instruments employed would be very considerable and it is not safe to assume the correctness of such instruments as they occur in trade.

The empirical method is as follows :

A sample of potassium nitrate is purified until it shows the absence of impurities by the ordinary tests. It is then dried and the nitric oxide derived from a known quantity, is passed into the measuring tube. The quantity of air in the reduction tube is then varied until the volume of the nitric oxide is approximately that calculated from the amount of nitrate taken. The reduction tube is now sealed and a series of analyses of potassium nitrate made with slight variations in the amount taken, and in each case a correction factor determined which shows 100 per cent. in purity in the nitrate taken (see example below). The extreme variations in the determinations should not exceed 0.05 per cent. From this series of determinations a correction factor is calculated which is applied to all determinations.

EXAMPLE.

0.5078 gram KNO₃ gave 111.7 cc. nitric oxide.

Log. 111.7	0.04805
Log. 0.5078	0.70569

Log. of cc. per gram 0.34236

0.5057 gram KNO₃ gave 111.2 cc. nitric oxide.

Log. cc.....	0.04610
Log. s.....	0.70389
	0.34221

0.5058 gram KNO₃ gave 111.2 cc. nitric oxide.

Log. cc.....	0.04610
Log. s.....	0.70398
	0.34212

The average of these logarithms gives : Log. cc. per gram 0.34223, corresponding to 219.9. The correction is obtained by the proportion 221.0 : 219.9, the first term being the theoretical cubic centimeters per gram for potassium nitrate.

Log. 221.0.....	0.34428
Log. 219.9.....	0.34223
	0.00205

In other words in any analysis the mantissa of the logarithm representing the cubic centimeters per gram or the percentage of nitrogen must be increased by 0.00205.

EXAMPLE.

0.5913 gram guncotton gave 119.1 cc. of nitric oxide.	
Log. cc.....	0.07591
Log. s.....	0.77181
	0.30410
	0.00205
	0.30615

This corresponds to 202.3 cc. per gram or 12.71 per cent. nitrogen.

The advantage of this method lies in the fact that all the sources of constant errors A to E are eliminated, no thermometer nor barometer being needed. The weights may be inexact if only consistent. The graduation of the tubes may be inexact and inconsistent. In fact they could be grossly inaccurate without affecting the accuracy of the results if separate corrections were made for each point on the measuring tubes.

The obvious objection to the method lies in the difficulty of preparing a pure potassium nitrate which shall not have a low content of nitrogen by reason of the presence of foreign matter nor a high content of nitrogen from the presence of sodium nitrate. These objections may be met by preparing samples of potassium nitrate from different sources. All should show the same percentage of nitrogen. Secondly, a sample of nitrate of soda should be purified and the correction factor determined from it independently. Within the limits of experimental error it should be the same as the correction factor derived from potassium nitrate.

EXAMPLE.

0.4302 gram sodium nitrate gave 112.5 cc. nitric oxide.	
Log. cc.....	0.05115
Log. s.....	0.63367
	0.41748
Log. theoretical cc. per gram for sodium nitrate	0.41954
	0.00206

As a third check a sample of pure dry nitroglycerine may be used.

At one time in my work the reduction tube was set by aid of a barometer, since shown to be faulty. A sample of potassium nitrate carefully purified showed in this case about 99 per cent. purity and a sample of sodium nitrate also carefully purified showed the same percentage of purity within the limits of error. The barometer setting of the reduction tube was therefore discarded and the correction factor introduced since it was manifest that, while either of the nitrates might be impure even after the most careful purification, it was in a high degree improbable that both should be impure and of exactly the same degree of impurity.

During the hot weather of summer there is a distinct advantage in having a large subtractive correction factor. In this way the gas may be measured nearly at the pressure of the atmosphere, thus avoiding the considerable strain on the stop-cock and consequent tendency to leakage.

The nitric oxide may be measured either dry or moist, more conveniently, however, in the latter condition. If so measured a few drops of water should be left in each tube. As the tension of the aqueous vapor is the same in each tube, it may be neglected in the calculations.

The sulphuric acid used in nitrometer work should be free from oxides of nitrogen and iron. It should be of 94 to 95 per cent. strength. In acid of 98 per cent. strength nitric oxide is quite freely soluble.

CALIFORNIA POWDER WORKS,
April, 1901.

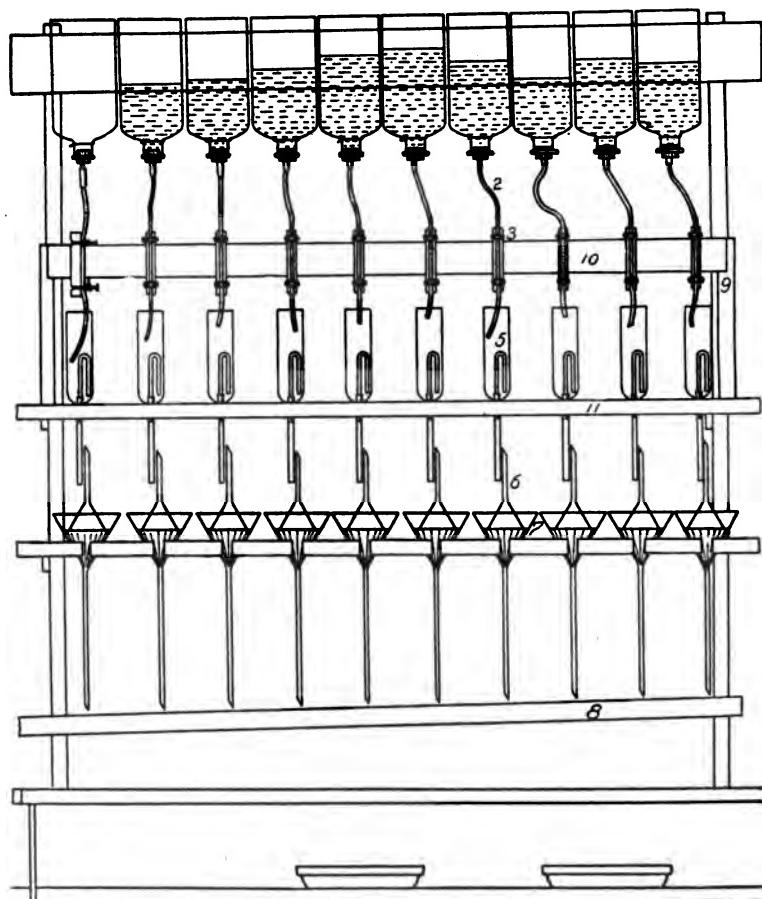
AN AUTOMATIC FILTER-WASHER.

BY J. M. PICKEL.

Received June 11, 1901.

THE apparatus shown in the accompanying cut, consists of a battery of ten washers. The parts of each washer are : A reservoir, 1, to contain the liquid with which the washing is done. A rubber tube, 2, provided with two thumb-screw clamps, 3, leading from the reservoir to the delivery vessel. A delivery vessel, 5, provided interiorly with a small siphon, which delivers the washing liquid intermittently in small portions on the substance being washed. A larger funnel, 7, containing the filter. A smaller inverted funnel, 6, covering the substance. The object of this funnel is, while it prevents spattering, to throw the liquid around

over the edge of the filter-paper, thus insuring that it be washed from the top downward at each delivery. It should be of such a diameter as almost, but not quite, to cover the filter-paper. A trough, δ , which conveys the washings, in case they are not wanted, into the waste pipe. A supporting frame, g , 10 , 11 .



The apparatus is operated thus: The substance to be washed having been placed on the filters and covered with the inverted funnels, and the lower clamps having been closed, each reservoir is provided with a measured quantity of liquid adequate to the washing. To facilitate the measuring, the reservoirs should be graduated once for all. By means of the lower clamp discharge

the liquid rapidly into the delivery vessel until the siphon overflows, then regulate (by the *lower* clamp) the flow so that the liquid shall fall, drop by drop, into the delivery vessel at such a rate that the siphon shall not overflow till after all the liquid has passed out of the filter. This regulation insures the intermittent washing of the filter with entirely fresh portions of liquid at each delivery, and, with a little practice and patience, can be accomplished in about ten to fifteen minutes for all ten of the washers. After the apparatus is once regulated, it requires no further attention—may be left going over night.

The upper clamp is not necessary, but is at times convenient; for example, if for any reason it is desired to stop the flow of liquid before the washing is completed, this is effected preferably by the upper clamp, thus leaving the "set" of the lower clamp undisturbed. The efficiency of the machine depends upon the ease and accuracy with which it may be regulated. The screw of the regulating clamp must, therefore, have a fine thread; the clamp must be firmly fixed in place, otherwise the merest touch will sometimes change the rate of flow. The washer at the extreme left of the cut shows a method of securing this fixedness. The clamps and attachment are there turned through an angle of 90°. A piece of wood about two inches long and of rectangular section passes through the clamp. Transversely across the back of the piece of wood are shallow grooves in which the clamps fit. These pieces are firmly attached by screws to the frame-piece marked *ro*. Small wire brads, one just above and one just below the clamp, and each slightly pressing against it, are driven a short way into the wood completing thus the steadiness of the clamps. The arrangement here described is satisfactory; but doubtless a tube and glass cock, capable of delivering small drops (after the manner of a good burette), would be preferable.

The quantity of water delivered at each discharge of the siphon should, of course, be sufficient to cover the substance but not enough to flood the filter to overflowing. The capacity of the delivery vessel may be varied by adding to or taking from it, small glass beads, coarse sand, or fragments of glass. It is evident that, if the siphon is on the outside of the delivery vessel (after the manner of a Soxhlet extractor), the capacity of the vessel may easily be varied from its greatest volume down to an almost vanishing quantity by shoving

down into it a tube closed at its lower end (a test-tube for example); a small plug of rubber wedged in between would hold the tube at any desired level. A Soxhlet can be utilized as a delivery vessel; one, in possession of the writer, whose normal maximum delivery is 43 cc. can, in the manner just described, be instantly made to deliver any lesser quantity down to 7 cc.

As is seen from the cut, the delivery vessels in the apparatus here described are what are known as carbon filters, for Gooch filters. Their dimensions are, for the large end, about 2 to 3 inches in length and $\frac{1}{4}$ -inch internal diameter, small or stem end, about 2 inches in length and $\frac{1}{4}$ -inch internal diameter. The long arm of the siphon passes through the stem and is made watertight by a short piece of rubber tubing. They were regulated once for all to deliver about 10 to 15 cc. The siphons should be well made, particular care being taken that they are not flattened, or contracted, at the bend. A siphon thus contracted requires, especially when it becomes somewhat soiled internally and does not readily wet, considerable pressure to force the water over; it will therefore vary considerably in the volume of liquid that it delivers at an overflow. For this reason also a narrow tall delivery vessel is to be preferred to one of larger diameter—there is less variation in the quantity of liquid delivered at each overflow of siphon in the former than in the latter. A diameter (internal) of not over an inch—of even three-quarters of an inch or less if practicable—is to be recommended. I especially call attention to this, because I found that some of my delivery vessels, which were set to deliver about 10 cc. would, owing to the causes here detailed, sometimes cause my filters to overflow (I was using quite small, 9 cm. filters). The reservoirs in this apparatus were made by cutting off, near the bottom, pint bottles. Small percolators would be neater.

The combination here described as an automatic filter-washer is, so far as the writer knows, new. At any rate, it was new to him and devised by him for washing water-soluble nitrogen (more especially nitric and ammoniacal nitrogen) out of mixed commercial fertilizers. It was used the past winter and spring for that purpose in the analysis of several hundred samples, and was found entirely satisfactory and a valuable labor-saver. Two nitrogen determinations were made in each case, one of total nitrogen, the other of residual nitrogen after washing with 300 cc. of distilled water.

There would seem to be no reason why this washer might not be used, with equal advantage, to take water-soluble phosphoric acid out of commercial fertilizers. A comparison of its work in this matter with the method of washing commonly practiced, was made with the following result on ten different fertilizers :

	Per cent.									
	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Water-soluble P ₂ O ₅ .	6.65	4.55	9.51	9.31	8.04	9.24	5.97	6.10	5.06	6.00
" "	6.42	3.78	8.92	8.75	7.88	8.65	6.10	5.68	4.72	5.42
Difference.....	0.23	0.77	0.59	0.56	0.16	0.59		0.42	0.34	0.58

The percentages in the top line were obtained in the washings from the automatic washer; those in the second line were obtained in the usual way by directing a jet of water on the substance and thoroughly stirring up at each washing. Two grams of fertilizer were taken in each case, and the same quantity (or about the same quantity), a little less than 300 cc. of water, was used for washing in each case. In all except one case, the automatic washer took out more phosphoric acid than the usual method. This is all the more remarkable inasmuch as the washer does not stir the substance to any appreciable extent. The explanation of the difference is perhaps to be found in this circumstance; the washer delivered the water in small portions of about 10 cc. at a time, whereas in the other case 30 to 40 cc. were used, the filter being larger; it thus came about that in the first case the samples got three to four times as many separate washings as in the second. There was this further circumstance: The machine, once set going, keeps up the work to the end, thus finishing the operation in a shorter time than did the hand washing, where the chemist was diverted by other operations which he was looking after at the same time. Such being the case, the phosphates were in contact with the water a shorter time in the first than the second instance, and the monocalcium phosphate had less opportunity (less time) to "revert."

ANALYTICAL AND CONSULTING LABORATORY OF
DR. J. M. PICKEL, RALEIGH, N. C.,
June, 1901.

[CONTRIBUTION FROM THE LABORATORY OF THE UNIVERSITY OF MINNESOTA.]

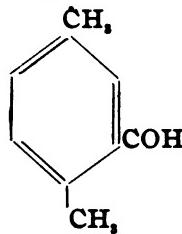
PREPARATION OF 2,5-DIMETHYLBENZALDEHYDE; THE ESTABLISHMENT OF ITS CONSTITUTION AND PREPARATION OF SOME OF ITS DERIVATIVES.

BY EVERHART P. HARDING AND LILLIAN COHEN.

Received July 5, 1901.

FEW compounds have offered a more interesting study than the aromatic aldehydes. This is due not to their theoretical value alone but to their utilitarian value as well. Gattermann¹ says that in all known aldehydes (containing one or more methyl groups in the benzene ring) prepared by the Gattermann-Koch method,² the aldehyde group always occupies the *p*-position relative to a methyl group.³ The object of this paper was to determine whether the aldehyde could enter the benzene ring without occupying a *p*-position to any of the methyl groups which resulted in the preparation of 2,5-dimethylbenzaldehyde, the establishment of its constitution and the preparation of some of its derivatives.

PREPARATION OF 2,5-DIMETHYLBENZALDEHYDE.



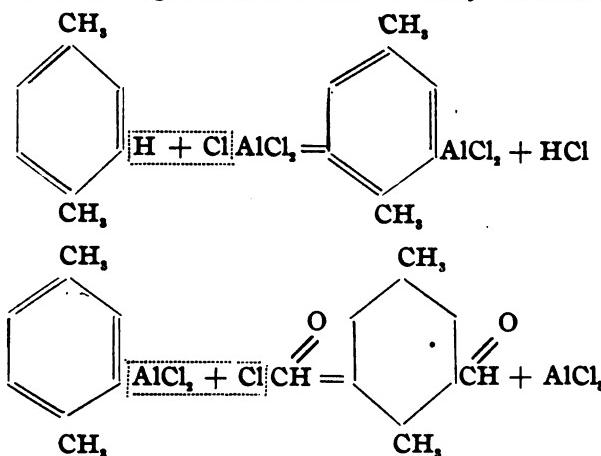
2,5-Dimethylbenzaldehyde was prepared according to the Gattermann-Koch method,³ which depends upon the action of the hypothetical formyl chloride upon aromatic hydrocarbons in the presence of aluminum and cuprous chlorides. The temperature of the xylene mixture was kept at 40° and the time required for the thickening of the mass varied from five to ten hours, depending upon the quality of the aluminum chloride used. The double compound of aldehyde and aluminum chloride was decomposed by transferring to a flask containing ice and the aldehyde and

¹ Ber. d. chem. Ges. 30, 1622.

² Ibid., 30, 1622; Wilhelm Graf: Inaug. Dissertation, 1899, Universitäts Buchdruckerei von J. Horning, Heidelberg; J. prakt. Chem. Neue Folg., 62, 1900.

³ Ber. d. chem. Ges. 30, 1622.

unchanged xylene removed by steam distillation and taken up with ether. After removing the ether by distillation, the residue was subjected to repeated fractional distillation. The aldehyde distilled over at 219° - 229° (uncorr.) as a colorless liquid which quickly turned to light yellow, due to its ready oxidation.



The aldehyde does not form an addition product with a saturated solution of sodium bisulphite¹ which makes the usual method of purifying the aldehydes by their conversion into the corresponding bisulphite compounds impracticable. The aldehyde was dissolved in very weak alcohol and then shaken for two days in a shaking machine with a saturated solution of pure sodium bisulphite dissolved in water.

The analysis gave :

0.1400 gram of the substance burned with cupric oxide gave 0.4140 gram carbon dioxide and 0.0933 gram water, equivalent to 0.1129 gram carbon and 0.0140 gram hydrogen.

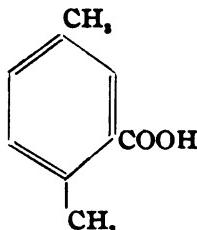
	Calculated for $\text{C}_9\text{H}_{10}\text{O}$.(134).	Found.
Carbon	80.59	80.64
Hydrogen	7.46	7.42

2.5-Dimethylbenzaldehyde is a colorless liquid with the characteristic benzaldehyde odor. It oxidizes very readily. Upon distillation a residue remains which, upon cooling, crystallizes in colorless needles. On exposure to the air it changes to a light yellow color and subsequently to prismatic needles which melt at

¹ The yellow commercial sodium bisulphite was not obtainable and consequently not tried.

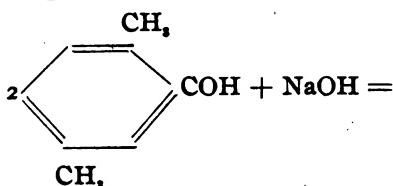
the melting-point of the corresponding acid.¹ It oxidizes so readily that upon distillation, air must be excluded from the apparatus and the distillate quickly cooled in ice-water. It is soluble in all the common solvents except water.

PREPARATION OF 2,5-DIMETHYLBENZOIC ACID.

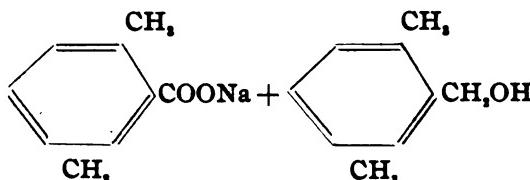


By the oxidation of 2,5-dimethylbenzaldehyde to the corresponding acid the position assumed by the aldehyde group in the benzene ring and consequently the constitution of the aldehyde was determined.

Since chromic acid and potassium permanganate oxidize the methyl group as well as the aldehyde group a strong solution of sodium hydroxide was used. Two grams of 2,5-dimethylbenzaldehyde and a cold solution of 1.8 grams of sodium hydroxide dissolved in 1.5 grams water were placed in a well-stoppered bottle. The bottle was placed in a shaking machine and shaken until a permanent emulsion was formed. After standing for several days this hardened to a yellow solid. The corresponding alcohol and the sodium salt of the corresponding acid were formed. The alcohol was removed by treating with water and extracting with ether. Upon acidifying the aqueous solution with dilute hydrochloric acid the 2,5-dimethylbenzoic acid separated as a white crystalline precipitate. Recrystallized from 50 per cent. alcohol it melted at 124°-125° (uncorr.). A 50 per cent. alcoholic solution was boiled with animal charcoal and filtered. The precipitate formed on cooling melted at 124°-125°.



¹ See 2,5-dimethylbenzoic acid.



The analysis gave :

0.1006 gram burned with cupric oxide gave 0.2657 gram carbon dioxide and 0.0585 gram water equivalent to 0.07246 gram carbon and 0.0065 gram hydrogen.

	Calculated for $C_9H_{10}O_2(150)$.	Found.
Carbon	72.00	72.02
Hydrogen.....	6.66	6.46

2,5-Dimethylbenzoic acid forms colorless needles of the mono- or triclinic system. $\angle \beta = 58^\circ 21'$.¹

External angle measured on $o1o = 48^\circ 36'$.

- $\infty a : \infty c = o1o =$ clinopinacoid.
- $a : b : \infty c = 110 =$ prism.
- $\infty a : \infty b : c = o01 =$ basal pinacoid.
- $a : \infty b : \infty c = 101 =$ orthopinacoid.

These crystals are soluble in methyl alcohol, ethyl alcohol, toluene, xylene, benzene, chloroform, and acetone. They are insoluble in cold and hot water. When boiled with pure animal charcoal and 50 per cent. alcohol, the filtrate turns slightly blue; the same blue color is observed during combustion.

If the aldehyde group always occupied the para position relative to a methyl group and if it were possible for the aldehyde group to exchange positions with one of the methyl groups, one of four acids of the corresponding aldehydes, *viz.*, *p*-tolyl acet-aldehyde, 2.4-, 3.4-, or 2,5-dimethylbenzoic acid, might have formed.

Paratolylacetic acid oxidizes with chromic acid to terephthalic acid and has a lower melting-point than that found.² 2,4- and 3,4-dimethylbenzoic acids also have different melting-points and different physical properties. Jacobson³ prepared an acid,⁴ which he called *p*-xylic acid, by the action of monobromparaxylene upon amalgam and phosgene and which melted at 132° . He also obtained a *p*-xylic acid which melted at 163° . Fittig and

¹Kindly determined by Dr. Berkey.

² *Ber. d. chem. Ges.*, 18, 1744; 42, 1882.

³ *Ibid.*, 1888, p. 1933; 22, 1230; 20, 2051; 18, 1281.

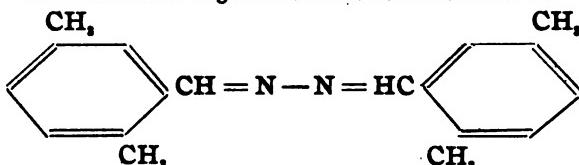
⁴ *Ibid.*, 14, 2111; 17, 2374.

Laubinger¹ prepared an acid by oxidizing pseudocumene with dilute nitric acid which melted at 163°, and which they called *p*-xylic acid.

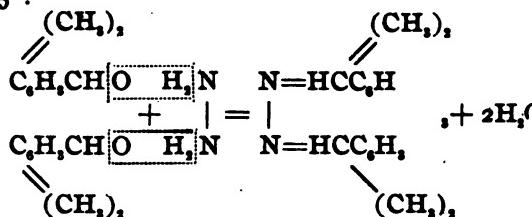
In all probability the so-called *p*-xylic acid melting at 163° obtained by Jacobson, and the acid obtained by Laubinger and Fittig melting at 163°, are the orthoxylic acid recently obtained by Graf² by treating orthoxylic aldehyde with strong potassium hydroxide and which melted at 163°. A further proof that the acid formed is neither 2.4- nor 3.4-dimethylbenzoic acid is shown in this paper by the comparison of the melting-points of their corresponding cinnamic acids.

This proves that the aldehyde group does not occupy a para position relative to one of the methyl groups but a meta position to one and an ortho position to the other group.

ALDAZINE OF 2.5-DIMETHYLBENZALDEHYDE.



The aldazine of 2,5-dimethylbenzaldehyde was prepared according to the method of Curtius and Jay.³ Five grams of aldehyde dissolved in dilute alcohol was added to a solution of 2.5 grams hydrazine sulphate dissolved in an excess of water. By violent shaking in a shaking machine a light yellow precipitate formed which, when filtered off, washed consecutively with water and cold alcohol, and recrystallized from hot alcohol, melted at 114°-114.5°.



The analysis was:

0.1091 gram burned with cupric oxide gave at 24° and 741 mm., 10.8 cc. saturated nitrogen gas equivalent to 11.799 mg. nitrogen.

¹ Ann. Chem. (Liebig), 181, 273.

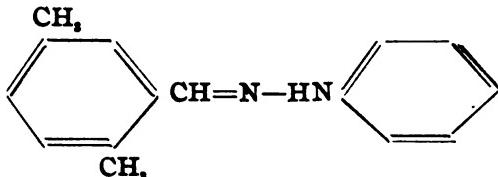
² Wilhelm Graf: Inaug. Dissertation, 1849, Universitäts Buchdruckerei von J. Hörring, Heidelberg.

³ J. prakt. Chem., Neue Folge, 89, 43.

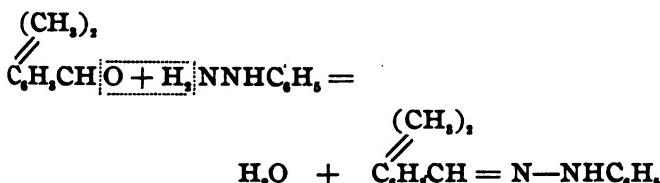
	Calculated for $C_{15}H_{20}N_2$ (224).	Found.
Nitrogen.....	10.60	10.81

The aldazine of 2.5-dimethylbenzaldehyde is soluble in methyl and ethyl alcohols, ether, benzene, toluene, xylene, and glacial acetic acid. It is insoluble in water.

PHENYLHYDRAZONE OF 2.5-DIMETHYLBENZALDEHYDE.



Five grams of 2.5-dimethylbenzaldehyde dissolved in an equal weight of alcohol were added to a mixture of 1.8 grams of phenylhydrazine dissolved in a mixture of two grams of glacial acetic acid and an equal volume of water. Upon shaking, the hydrazone separated as a yellowish-white precipitate which, filtered, washed consecutively with water and cold alcohol, and recrystallized from glacial acetic acid, melted at 84° - 85.5° .



It is necessary to conduct this experiment quickly, as the hydrazone is very unstable. The crystals soon turn a yellowish brown and subsequently a deep red. This red color appears when an alcoholic solution of the hydrazone stands for some time; also when the hydrazone is placed in an exhausted desiccator.

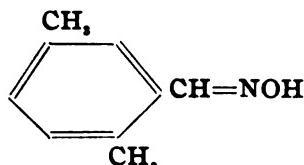
Analysis :

0.0542 gram burned with copper oxide gave at 17° and 750 mm., 6 cc. of saturated nitrogen gas, equivalent to 6.870 mg. nitrogen.

	Calculated for $C_{15}H_{14}N_2$ (224).	Found.
Nitrogen.....	12.50	12.67

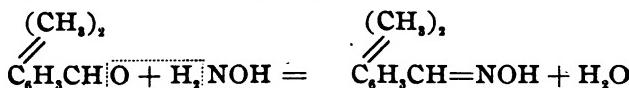
Hydrazone of 2.5-dimethylbenzaldehyde is soluble in ethyl and methyl alcohols, ether, benzene, toluene, and xylene. It is insoluble in water.

OXIME OF 2,5-DIMETHYLBENZALDEHYDE.



Two grams of 2,5-dimethylbenzaldehyde were dissolved in 15 grams of alcohol. To this solution was added a solution of 1.8 grams of hydroxylamine hydrochloride in 5 grams of water and subsequently a solution of 4.5 grams of potassium hydroxide in 5 grams of water. The mixture was placed in a small round-bottomed flask, provided with a reflux condenser and heated for two hours upon a water-bath. The alcohol was then partially evaporated and the solution poured into 50 grams of water and filtered to remove any unchanged aldehyde. The free oxime was then precipitated by the addition of dilute hydrochloric acid. The colorless crystalline precipitate was filtered off, pressed upon an unglazed porcelain plate and recrystallized from 40 per cent. alcohol.

The crystals melted at 83.5° - 84° .



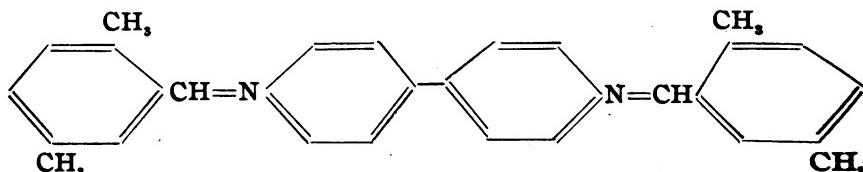
Analysis :

0.0939 gram burned with cupric oxide gave at 19° and 744 mm., 8 cc. saturated nitrogen gas, equivalent to 8.752 mg. nitrogen.

	Calculated for $C_9H_{11}NO(149)$.	Found.
Nitrogen.....	9.39	9.32

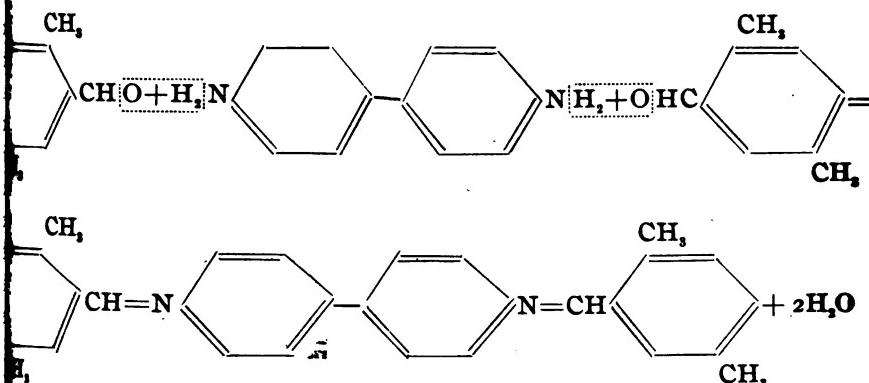
The oxime is soluble in ethyl and methyl alcohols, ether, benzene, toluene, xylene, and acetic acid. It is insoluble in water.

BENZIDINE DERIVATIVE OF 2,5-DIMETHYLBENZALDEHYDE



0.75 gram benzidine were dissolved in 5 grams warm alcohol.

in a small flask. To this was added 1 gram 2,5-dimethylbenzaldehyde dissolved in two grams alcohol. The contents of the flask were gently warmed until a yellow crystalline precipitate was formed. This was filtered off by means of a filter-pump, washed well with alcohol, and recrystallized several times out of toluene. The crystals melt at 187.5° uncorrected temperature, to an opalescent liquid which remains unchanged at 330° . The condensation takes place according to the following equation :



Analysis :

0.08495 gram of the substance burned with cupric oxide gave at 26° and 746 mm., 5.6 cc. nitrogen equivalent to 6.0564 mg. nitrogen.

	Calculated for $C_{30}H_{26}N_2(416)$.	Found.
Nitrogen	6.73	7.12

I. The crystals appear to be orthorhombic. Combination forms are chiefly a pyramid and a pinacoid.

II. The axial ratios are approximately :

$$a : b : c = 0.5255 + : 1 : \text{approximately } 1 + .$$

III. Axes b and c are very nearly the same length.

Assuming the pinacoid as basal, the forms are

$$(1) a : b : c = 111.$$

$$(2) a : b : c = 001.$$

One prism plane was noticed on one crystal.

$$a : b : c = 110.$$

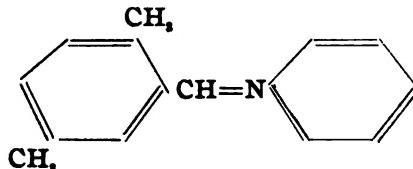
IV. The crystal is pleochroic, greenish yellow to yellowish green, showing greatest absorption parallel to axis b .

The crystals of the benzidine condensation, which are of a

sulphur-yellow color and very large, are soluble in benzene, toluene, xylene, chloroform, slightly soluble in acetone and benzine.

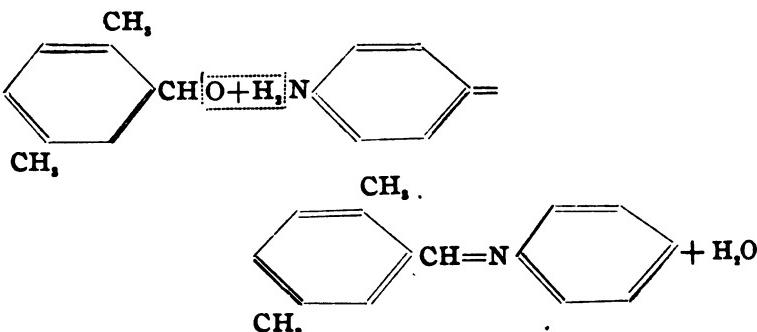
They are insoluble in methyl alcohol, ethyl alcohol, ether, hot and cold water.

ANILINE DERIVATIVE OF 2,5-DIMETHYLBENZALDEHYDE.



1.4 grams freshly distilled aniline were placed in a small round-bottomed flask; to this, 1 gram aldehyde was added, and the mixture heated for three hours on a water-bath. Then the substance, a golden brown liquid, was allowed to stand several days. Upon placing the flask into ice-water, crystals with a yellow tinge separated out. These, recrystallized from not too dilute alcohol, melted at 51° uncorrected temperature.

If too dilute alcohol is used the condensation product breaks up into its original constituents. The reaction is analogous to that of the benzidine condensation.



Analysis:

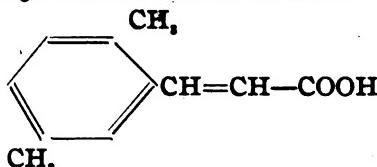
0.0410 gram of the substance burned with cupric oxide at 29° and 752 mm., gave 2.5 cc. nitrogen, corresponding to 2.77 mg. nitrogen.

	Calculated for $C_{15}H_{18}N(209)$.	Found.
Nitrogen.....	6.69	6.78

The crystals form glancing plates very soluble in ether, methyl alcohol, ethyl alcohol, benzene, toluene, xylene, and benzine.

Water decomposes the compound very easily, forming aniline and aldehyde.

2.5-DIMETHYLCINNAMIC ACID.



1.25 grams freshly distilled aniline were placed in a round-bottomed flask, and to this 1 gram redistilled 2,5-dimethylbenzaldehyde was added. The flask was provided with a safety-tube about two feet long, which prevented the entrance of any moisture.

The mixture was boiled three hours on a water-bath ; then the temperature was raised a little above 100°.

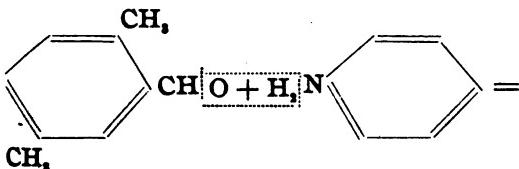
One gram malonic acid dried at 100° for one hour was dissolved in absolute alcohol and added to the solution.

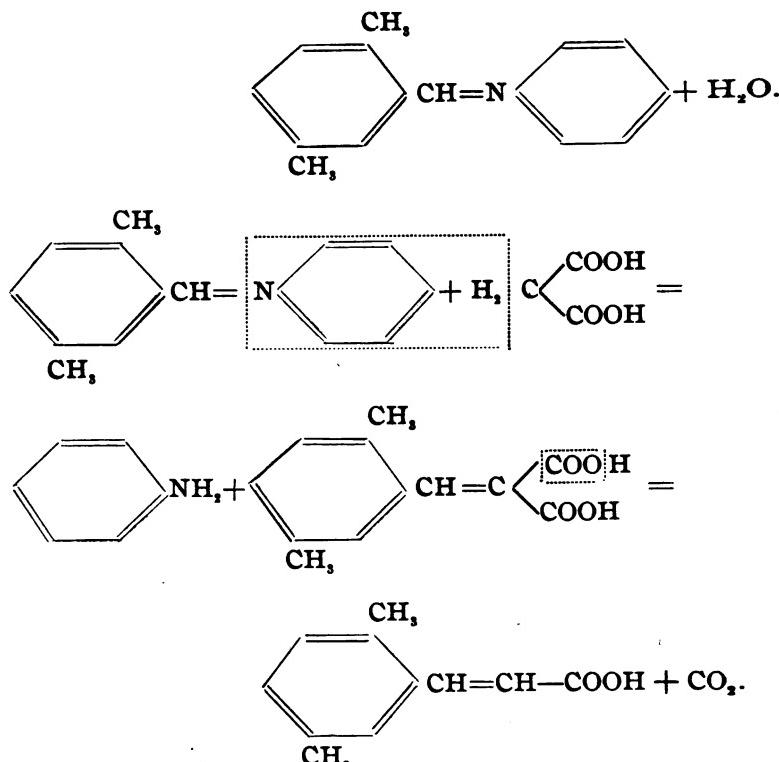
The golden brown liquid was allowed to stand over night, the safety tube being plugged to keep out the moisture.

In the morning a light colored crystalline mass formed, which contained no trace of the green color often formed as a by-product.

In order to remove the aniline set free in the reaction, 3 grams of concentrated hydrochloric acid diluted with 3 grams water were added, and the substance was allowed to stand three-quarters of an hour. At the end of this period, the aniline hydrochloride was filtered off, and the residue washed with water until the wash-water remained clear. The residue was then thoroughly extracted with hot benzine. White needles crystallized out of the benzine solution, which melted at 176.5° uncorrected temperature, when recrystallized out of alcohol.

The yellow substance remaining in the flask was a dye, which dissolved in alcohol to a red-green fluorescent liquid. This was formed as a by-product.





Analysis :

0.1440 gram burned with cupric oxide gave 0.3970 gram carbon dioxide and 0.0872 gram water; equivalent to 0.10827 gram carbon and 0.00968 gram hydrogen.

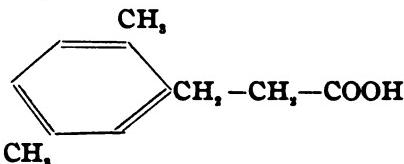
	Calculated for $\text{C}_{11}\text{H}_{12}\text{O}_2(176)$.	Found.
Carbon.....	75	74.98
Hydrogen	6.81	6.71

The crystals belong to the triclinic system and have indefinite faces. The extinction angle is high.

2,5-Dimethylcinnamic acid is soluble in methyl alcohol, ethyl alcohol, ether, chloroform, benzine, benzene, toluene, xylene, and acetone. It is insoluble in cold water, but soluble in a great excess of hot water.

2,5-Dimethylcinnamic acid acts as an unsaturated compound, forming with bromine a brom compound and with hydrogen a hydrocinnamic acid.

2.5-DIMETHYLHYDROCINNAMIC ACID.

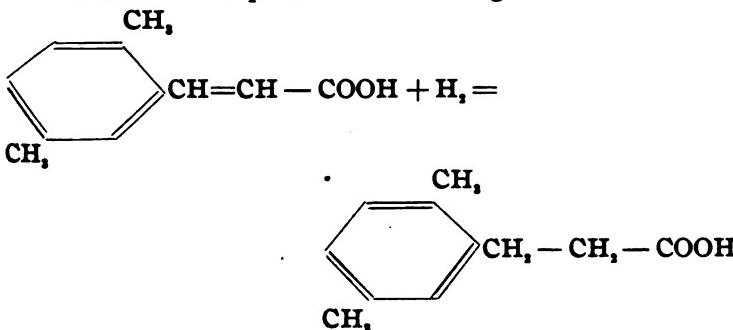


Two grams dimethylcinnamic acid were treated in a small flask with 2 grams water and sufficient dilute sodium hydroxide was added to render the solution clear and weakly alkaline. The sodium salt of the cinnamic acid which is soluble in water was formed.

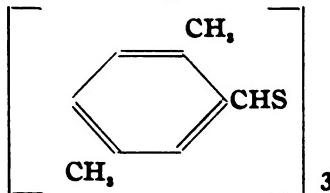
To form the hydro compound 2 grams of 4 per cent. sodium amalgam were added very gradually in order to utilize all the hydrogen generated. When all the mercury had been set free the contents of the flask were gently warmed on the water-bath, and then the mercury was filtered off.

Dilute hydrochloric acid was added to the filtrate until all the acid was separated out as a white precipitate. This was filtered, pressed, and dried on a porous plate, and crystallized twice from benzene. The needle-shaped crystals melt at 111.5° uncorrected temperature.

The reduction takes place in the following manner :



TRITHIO DERIVATIVE OF 2.5-DIMETHYLBENZALDEHYDE.



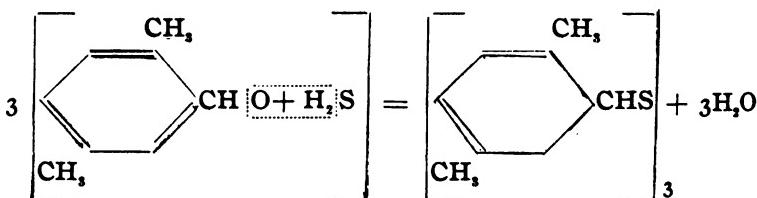
One gram 2.5-dimethylbenzaldehyde was dissolved in 7.5 grams absolute alcohol. Three grams of concentrated hydrochloric acid were added to this solution. A rapid stream of hydrogen sulphide was passed through this mixture three and a half hours at room temperature.

The solution first turned blue, due to formation of the mono-thio derivative, then a white precipitate separated out, and at the end of the reaction a pinkish yellow adhesive mass mixed with a predominant amount of a chalk-like precipitate had formed.

The supernatant liquid was poured off, the residue thoroughly washed with alcohol and then pressed and dried on a porous plate.

The substance dissolved in benzene would not crystallize. A crystal of iodine was then added to the solution, which was then allowed to stand several weeks, when large colorless plates of the monoclinic system separated out. These were recrystallized from absolute alcohol.

Melting-point = 110° uncorrected temperature. The thio derivative is a polymer.



Owing to the small amount of the pure substance obtained, no combustion was made, but the molecular weight was determined by the depression of the freezing-point.

Weight benzene used. Grams.	Weight of substance used. Gram.	Substance in solution. Per cent.	Freezing-point of solvent. 3.80	Freezing-point of substance. 3.84
11.2186	0.0522	0.46		

$$\text{Depression} = 0.04.$$

Calculated for
 $(\text{C}_9\text{H}_{10}\text{S})_3$.
450

Found.
453.7

The crystals are soluble in benzene, absolute alcohol, chloroform and insoluble in water. They possess the peculiar characteristic odor of the aromatic thioaldehydes.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
No. 59.]

THE ELECTROLYTIC METHOD APPLIED TO URANIUM.

BY LILY GAVIT KOLLOCK AND EDGAR F. SMITH.

Received July 5, 1901.

THE purpose of the present communication is to call attention to the conditions under which uranium can be quantitatively determined in the electrolytic way in solutions of the acetate, the sulphate, and the nitrate, and also to record several separations of uranium by the same means from other metals. It is not necessary to comment further upon the form in which the uranium is precipitated or upon the way in which the deposit is subsequently treated in order to weigh it, as those points have received sufficient attention elsewhere.¹

ELECTROLYSIS OF URANIUM ACETATE.

	U ₃ O ₈ present in grams.	20 percent acetic acid. cc.	Dilution.	Current.	Voltage.	Temperature. °C.	Time. Hours.	U ₃ O ₈ found in grams.	Error in grams.
1	0.0986	0.2	125	N.D. ₁₀₇ = 0.29 A	16.25	70	5	0.0988	+ 0.0002
2	0.0986	0.2	125	N.D. ₁₀₇ = 0.3 A	12.2	70	5	0.0989	+ 0.0003
3	0.1972	0.2	125	N.D. ₁₀₇ = 0.55 A	13.5	70	4	0.1968	- 0.0004
4	0.1972	0.2	125	N.D. ₁₀₇ = 0.3 A	10.75	70	6	0.1970	- 0.0002
5	0.1972	0.2	125	N.D. ₁₀₇ = 0.135 A	5.5	70	5	0.0966	- 0.0006
6	0.2952	0.2	125	N.D. ₁₀₇ = 0.16 A	4.5	75	5	0.2946	- 0.0006
7	0.2952	0.1	125	N.D. ₁₀₇ = 0.1 A	4.5	70	7	0.2948	- 0.0004
8	0.2298	0.1	125	N.D. ₁₀₇ = 0.09 A	4.25	70	6	0.2297	- 0.0001
9	0.2298	0.2	125	N.D. ₁₀₇ = 0.07 A	4.25	70	5½	0.2299	+ 0.0001
10	0.2298	0.1	125	N.D. ₁₀₇ = 0.05 A	4.0	65	5	0.2299	+ 0.0001

It was hoped that possibly iron might be separated from uranium in the acetate solution. Direct experiment demonstrated the opposite. The basic iron salt invariably separated when the temperature of the solution rose to 50° C. Further, the presence of iron in the solution apparently retarded the precipitation of the uranium, as none of the hydroxide of the latter separated with a current of 0.18 ampere and 8 volts. On adding chrome alum to the uranium acetate solution containing 2 cc. of free acetic acid and increasing the voltage to 20, there occurred no

¹ *Am. Chem. J.*, 1, 329; This Journal, 20, 279; and Smith's "Electrochemical Analysis," p. 94.

deposition of uranic hydroxide; the chromic oxide on the other hand was converted into chromic acid.

THE ELECTROLYSIS OF URANYL NITRATE SOLUTIONS.

$\text{U}_{\text{3}}\text{O}_8$ present in grams.	Dilution. cc.	Temper- ature. °C.	Current. $\text{N.D.}_{107} = 0.03 \text{ A}$	Volt- age. 4.6	Time. Hours. $5\frac{1}{2}$	$\text{U}_{\text{3}}\text{O}_8$ found in grams. 0.1225
0.1222	125	75	$\text{N.D.}_{107} = 0.03 \text{ A}$	4.6	$5\frac{1}{2}$	0.1218

Quantitative results were also obtained by the electrolysis of the sulphate. The neutral salt solution was diluted to 125 cc. and heated to 75° C., when a current of from 0.02 to 0.04 ampere for 107 sq. cm. of cathode surface and 2.25 volts was passed.

ELECTROLYSIS OF URANYL SULPHATE.

$\text{U}_{\text{3}}\text{O}_8$ present in grams.	Dilution. cc.	Temperature. °C.	Current.	Voltage.	Time. Hours.	$\text{U}_{\text{3}}\text{O}_8$ found in grams.	Error in grams.
0.1320	125	75	$\text{N.D.}_{107} = 0.02 \text{ A}$	2	$6\frac{1}{2}$	0.1320
0.1320	125	75	$\text{N.D.}_{107} = 0.02 \text{ A}$	2	$5\frac{1}{2}$	0.1322	+ 0.0002
0.1393	125	75	$\text{N.D.}_{107} = 0.04 \text{ A}$	2.25	5	0.1395	+ 0.0002
0.1393	125	70	$\text{N.D.}_{107} = 0.038 \text{ A}$	2.25	7	0.1392	- 0.0001

THE SEPARATION OF URANIUM FROM BARIUM, CALCIUM, MAGNESIUM, AND ZINC.

In the paper by Smith¹ to which reference has already been made, he calls attention to the separation of uranium in the electrolytic way from the alkali metals and from barium. Actual results are given. It seemed desirable to amplify the suggestion; hence the presentation of the results given below. It may be said here, that in attempting to separate nickel and cobalt no satisfaction could be obtained, so that eventually that particular line of experiment was abandoned. During the precipitation of the urano-uranic hydrate the dish should be well covered so that as little evaporation as possible occurs. It was observed that in case of evaporation there was danger of other salts separating upon the exposed metal and on refilling with water the uranium precipitate was apt to enclose the same and thus carry with it a slight impurity. This precaution is especially necessary in the separation from zinc.

¹ Loc. cit.

SEPARATION OF URANIUM FROM BARIUM (ACETATES).

	U ₃ O ₈ present in grams.	Barium present in grams.	20 per cent. free acetic acid. cc.	Dilution. cc.	Temperature. °C.	Current.	Voltage.	Time. Hours.	U ₃ O ₈ found in grams.	Error in grams.
1	0.1116	0.11	0.5	125	70	N.D. ₁₀₇ = 0.02 A	2	5½	0.1119	+ 0.0003
2	0.1116	0.11	0.5	125	65	N.D. ₁₀₇ = 0.04 A	8	5½	0.1117	+ 0.0001
3	0.1116	0.11	0.2	125	70	N.D. ₁₀₇ = 0.1 A	4.5	4	0.1117	+ 0.0001

SEPARATION OF URANIUM FROM CALCIUM (ACETATES).

	U ₃ O ₈ present in grams.	Calcium pres- ent in grams.	20 per cent. free acetic acid. cc.	Dilution. cc.	Temperature. °C.	Current.	Voltage.	Time. Hours.	U ₃ O ₈ found in grams.	Error in grams.
1	0.1116	0.1	0.2	125	70	N.D. ₁₀₇ = 0.025 A	2.25	6½	0.1113	- 0.0003
2	0.1116	0.1	0.2	125	70	N.D. ₁₀₇ = 0.04 A	2.5	5½	0.1114	- 0.0002
3	0.1116	0.1	0.2	125	70	N.D. ₁₀₇ = 0.05 A	2.25	4½	0.1113	- 0.0003
4	0.1116	0.1	0.2	125	70	N.D. ₁₀₇ = 0.025 A,	2.0	4½	0.1115	- 0.0001

SEPARATION OF URANIUM FROM MAGNESIUM (ACETATES).

	U ₃ O ₈ present in grams.	Magnesium present in grams.	20 per cent. free acetic acid. cc.	Dilution. cc.	Temperature. °C.	Current.	Voltage.	Time. Hours.	U ₃ O ₈ found in grams.	Error in grams.
1	0.1116	0.1	0.1	125	70	N.D. ₁₀₇ = 0.026 A	2.25	6	0.1115	- 0.0001
2	0.1102	0.1	0.1	125	70	N.D. ₁₀₇ = 0.05 A	2.25	5½	0.1104	+ 0.0002
3	0.1120	0.1	0.1	125	75	N.D. ₁₀₇ = 0.15 A	4.0	4	0.1119	- 0.0001

SEPARATION OF URANIUM FROM ZINC (ACETATES).

	U ₃ O ₈ present in grams.	Zinc present in grams.	20 per cent. free acetic acid. cc.	Dilution. cc.	Temperature. °C.	Current.	Voltage.	Time. Hours.	U ₃ O ₈ found in grams.	Error in grams.
1	0.1120	0.1	0.1	125	70	N.D. ₁₀₇ = 0.021 A	2.25	6	0.1120
2	0.1102	0.2	0.2	125	70	N.D. ₁₀₇ = 0.017 A	2.25	6	0.1099	- 0.0003
3	0.1102	0.1	0.1	125	70	N.D. ₁₀₇ = 0.02 A	2.2	6	0.1100	- 0.0002
4	0.1102	0.1	0.2	125	75	N.D. ₁₀₇ = 0.025 A	4.4	4½	0.1103	+ 0.0001
5	0.1102	0.15	0.2	125	75	N.D. ₁₀₇ = 0.01 A	2.2	6	0.1105	+ 0.0003
6	0.1102	0.2	0.2	125	75	N.D. ₁₀₇ = 0.02 A	2.25	6	0.1099	- 0.0003

UNIVERSITY OF PENNSYLVANIA.

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THE SYNTHESIS OF ALKYL KETODIHYDROQUINAZOLINS FROM ANTHRANILIC ACID.

BY AUGUST HENRY GOTTHELF.

Received June 26, 1901.

THEORY.

It has been shown in two previous papers¹ that the action of nitriles upon anthranilic acid, when heated together under pressure, results in the formation of ketodihydroquinazolins; and in the second paper the preparation of 2-methyl-4-ketodihydro-

quinazolin (or *α*-methyl-*β*-quinazolon), $C_6H_4\begin{array}{c} N=CCH_3 \\ | \\ CO-NH \end{array}$, was

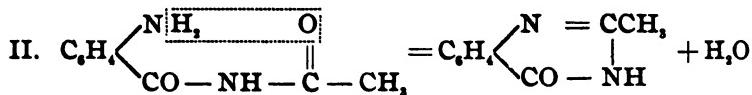
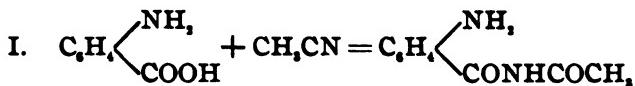
discussed in detail; both theoretically and practically. The present paper treats of the application of this method to the synthesis of higher members of the series; *viz.*, the ethyl, normal and isopropyl-, isobutyl-, and isoamylquinazolons, the last two being new; and also the preparation of several of their derivatives.

It has already been stated² that the addition of acetic anhydride was found very beneficial in the preparation of the methyl derivative and that the reactions thought most probable are as follows:

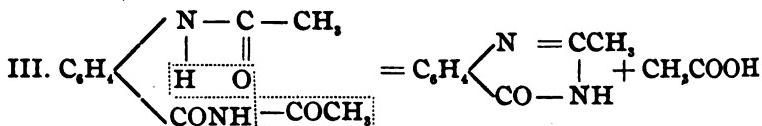
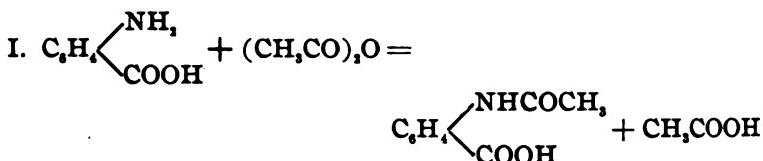
Without anhydride :

¹ Bogert and Gotthelf: This Journal, 22, 729 and 522.

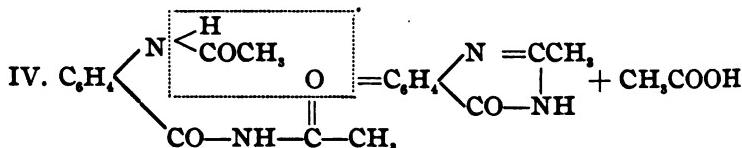
² This Journal, 22, 530.



With anyhydride :



or



In preparing the higher derivatives, various modifications of the process were tried in order to throw more light upon these reactions and to determine the conditions necessary for the best yield. These may be summed up as follows : Anthranilic acid was heated with :

I. Nitrile alone.

1. Propionitrile.
2. *n*-Butyronitrile.
3. Isovaleronitrile.
4. Isocapronitrile.

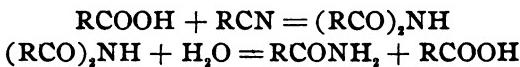
Nothing in confirmation of, or opposition to, the theory of this reaction as given above was discovered from these experiments. The yield varied, being very poor in some cases and good in others.

II. Nitrile and the corresponding acid anhydride.

1. Propionitrile and propionic anhydride.
 2. *n*-Butyronitrile and *n*-butyric anhydride.
 3. Isovaleronitrile and isovaleric anhydride.

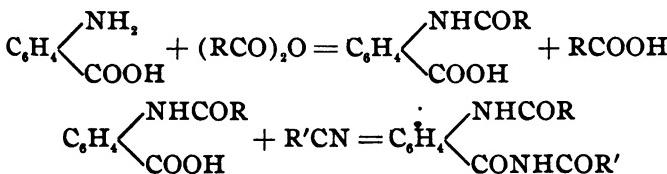
The addition of anhydride was found to greatly increase the yield in every instance. The reaction probably taking place under these conditions has already been shown. The rapid combination of the anhydride with the anthranilic acid was indicated in each case by the mixture becoming warm and solidifying almost immediately after mixing.

The by-products of the reaction are the anilide and amide of the fatty acid whose anhydride and nitrile are used. The former is found, however, only in those tubes which show considerable pressure on opening, and its formation is, therefore, probably due to the splitting off of carbon dioxide from the acylanthranilic acid. The presence of the amide can be explained by supposing a secondary amide to form in the tube by the interaction of the fatty acid and nitrile, which then, on heating with water in the after-treatment of the tube-contents, decomposes to the primary amide:

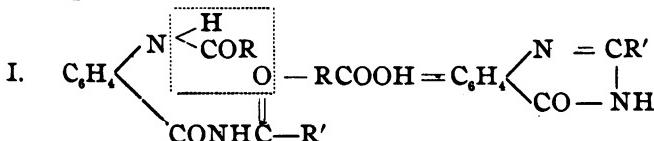


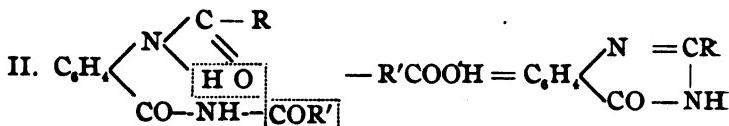
III. Nitrile and a different acid anhydride.

In the experiments thus far considered the formation of but one quinazolon was possible (excluding tautomeric forms), but when different anhydrides and nitriles are used, two may result, as shown by the following equations:



The reaction so far is the same as usual, but now, in forming the ring, either RCOOH or $\text{R}'\text{COOH}$ may split off, resulting in different quinazolons :





The reactions tried were:

A. Nitrile and a higher acid anhydride.

1. Acetonitrile and propionic anhydride.
2. Acetonitrile and *n*-butyric anhydride.
3. Acetonitrile and isobutyric anhydride.
4. Propionitrile and isobutyric anhydride.

In these cases the reaction always followed equation (II); *i.e.*, the anhydride determined which quinazolon was formed: (1) giving ethyl; (2) normal propyl; and (3) and (4) isopropyl quinazolon.

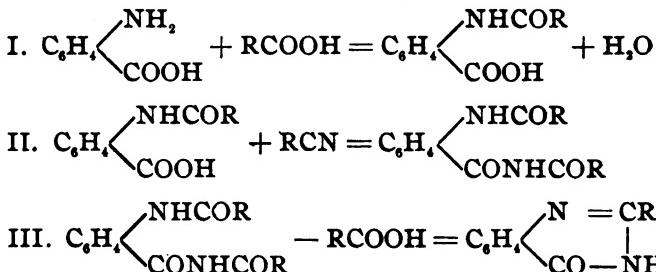
B. Nitrile and a lower acid anhydride.

1. Propionitrile and acetic anhydride.
2. Isocapronitrile and isobutyric anhydride.
3. Isocapronitrile and *n*-butyric anhydride.

Of these, (1) yielded pure methyl quinazolon and therefore reacted according to equation (II), while (2) and (3) yielded mixtures.

IV. Nitrile and the corresponding acid.

The reaction in this case, if it follows the same course as when anhydride is used, is as follows:



It does not seem likely, however, that, especially with the higher weaker acids, reaction (I) proceeds to any great extent, if at all, as it depends on the affinity between the fatty acid and the amino group of the anthranilic acid, an affinity which, among the higher acids, is practically zero. Experiments by the writer with normal butyric and isocaproic acids show that, under the

same conditions as to heat and pressure that existed in the tubes, these acids do not combine, to any appreciable extent, with anthranilic acid.

The nitriles and acids used were :

1. Acetonitrile and acetic acid.
2. Propionitrile and propionic acid.
3. *n*-Butyronitrile and *n*-butyric acid.
4. Isocapronitrile and isocaproic acid.

In these reactions the results were very similar to those of case (II), the yields being about the same and anilides and amides being found as by-products. The formation of the amide can be more simply explained in this case by the action of the liberated water on the nitrile. In order to allow for this saponification, two molecules of nitrile were used to one each of anthranilic acid and fatty acid. The anilides are doubtless due to the action of aniline, formed by the decomposition of anthranilic acid, on either the fatty acid or the amide.

V. Nitrile and a different acid.

As in the third case, so in this one, the formation of two quinazolons is possible. The reactions tried were :

A. Nitrile and a higher acid.

1. Acetonitrile and propionic acid.
2. *n*-Butyronitrile and capric acid.
3. Isocapronitrile and capric acid.

Of these, (2) and (3) gave pure quinazolons ; the former, the normal propyl, and the latter, the isoamyl derivative. The capric acid appears, therefore, to have taken no part in the reaction, probably because it is too weak to form any acyl derivative whatever with the anthranilic acid. Reaction (1), on the contrary, gave a product which was evidently a mixture.

B. Nitrile and a lower acid.

1. Acetonitrile and formic acid.
2. Propionitrile and formic acid.
3. Isocapronitrile and formic acid.
4. Isocapronitrile and propionic acid.

Reaction (4) resulted in pure isoamyl quinazolon and (3) in isoamyl quinazolon with a trace of what appeared to be 4-ketodi-hydroquinazolin itself, while (1) and (2) gave, apparently, no phenmiazine derivative at all.

In considering those reactions in which anhydrides or acids not corresponding to the nitriles were used, it will be seen that their course appears to depend both on the ease with which the anhydride or acid reacts with anthranilic acid to form acylan-thranilic acid, and on the molecular weights of the radicals introduced. Thus, under III, *A*, using nitrile and a higher anhydride, normal and isobutyric anhydrides were heated with acetic and propionic nitriles and in every case pure normal or isopropyl quinazolon resulted, while, under V, *A* (nitrile and a lower anhydride), the same anhydrides, when heated with isocaprononitrile, yielded mixtures. Evidently, in the latter case, the superior weight of the isocaproyl radical has exerted its influence and forced out the lighter radical as indicated in equation (I).

That the product also depends upon the relative strength of the acids and anhydrides is shown by the fact that, when using anhydrides, pure quinazolons, whose formulas depended upon that of the anhydride, were obtained in five instances, while, when using acids, in every case either a mixture resulted or the quinazolon obtained depended wholly upon the nitrile used. This is clearly shown by comparing reactions III, *A*, 1 and V, *A*, 1, in which propionic anhydride and propionic acid were heated with acetonitrile and yielded, respectively, pure ethyl quinazolon and a mixture.

To roughly determine the ease with which the higher fatty acids and anhydrides combine with anthranilic acid, a few experiments were performed, a description of which will be found at the end of this paper.

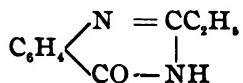
For purposes of comparison the melting-points of the quinazolons treated of in this paper are here tabulated. It will be noticed that they descend with the increase in molecular weight and that the isoderivatives melt much higher than the corresponding normal ones.

	Normal.	Iso.
Methyl.....	239°
Ethyl.....	234°
Propyl.....	199°-200°	230°-232°
Butyl.....	194°-195°
Amyl.....	184°

EXPERIMENTAL PART.¹

In all the following work the proportions of material used, unless specially mentioned, were the same in corresponding reactions; *i. e.*, when nitrile alone was used, two molecules were heated with one molecule of anthranilic acid; when acid anhydride was added, the proportions were one molecule nitrile, one of anhydride, and one of anthranilic acid; when a fatty acid was substituted for the anhydride, one molecule of fatty acid, two of nitrile, and one of anthranilic acid were used.

2-ETHYL 4-KETODIHYDROQUINAZOLIN.



Preparation.

I. Anthranilic Acid and Propionitrile.—The tube was heated to 170° – 180° for six hours and then to 200° – 210° for another six hours. After the first period the pressure was considerable but after the second it was slight. The tube-contents were dark-colored, completely crystalline, and smelled of ammonia. They were treated with cold sodium carbonate solution and the undissolved portion filtered out. The latter was then ground in a mortar with cold dilute caustic potash solution, the mixture filtered, the residue washed, and the quinazalon precipitated from the filtrate by passing carbon dioxide. The yield, after crystallizing once from water, amounted to $22\frac{1}{2}$ per cent. of the theoretical.

The residue from the caustic potash treatment was crystallized from water and found to be propionanilide, crystallizing in leaflets, melting at 104° - 105° , and yielding aniline when boiled with caustic alkali. It was probably formed by the action of aniline on propionamide, resulting in ammonia and propionanilide; as mentioned above, ammonia was found in the tube.

II. Anthranilic Acid, Propionitrile, and Propionic Anhydride.—This tube was heated to 160° – 170° and to 200° – 210° for six hours each, opening after each period. There was considerable pressure after the first heating and very little after the second, the tube contents consisting of a light brown homogeneous mass of

¹ All melting-points given, unless stated to be uncorrected, were determined with Anschütz short-scale thermometers, the entire mercury column being immersed in the heating liquid.

crystalline material. This was treated with cold sodium carbonate solution, and the residue extracted with alcohol, in which practically all dissolved. The alcoholic solution, after being decolorized with bone-black, was evaporated and the residue crystallized from water. The impure ethyl quinazolon thus obtained was separated from the propionanilide mixed with it by the use of cold dilute caustic alkali as described under (I). The yield was 31½ per cent.

With another tube the treatment with alcohol was omitted, the residue insoluble in sodium carbonate being warmed directly with dilute caustic potash for a short time. The solution was then cooled to permit the propionanilide to crystallize, filtered, and the quinazolon precipitated and purified as before. The yield in this case was 29 per cent.

The effect of an excess of anhydride and nitrile was also tried, a tube being prepared containing the substances in the proportion of 1½ molecules of anhydride and 2 of nitrile to 1 molecule of anthranilic acid. It was heated to 160°–170° for six hours and to 200°–210° for a similar period and yielded 30 per cent. of quinazolon.

III. Anthranilic Acid, Propionitrile, and Propionic Acid.—A tube containing these was heated to 160°–165° and to 200°–210° for five hours each. There was strong pressure after the first heating but little after the second, and the contents were light-colored and crystalline. They were treated successively with sodium carbonate and caustic potash solutions in the manner already described and the yield was 36 per cent. of the theoretical. Propionanilide was again a by-product.

Another tube containing the same amounts of material was heated to 150°–160° for five hours and to 175°–180° for five hours. The contents, after treatment with soda solution, were crystallized directly from water and yielded 28 per cent. of quinazolon.

IV. Anthranilic Acid, Acetonitrile, and Propionic Anhydride.—The tube was heated successively to 180°–190°, 220°–230°, and 225°–235° for five hours each. The pressure at any time was slight. After washing with soda solution the product was crystallized from water and a yield of about 17 per cent. of ethyl quinazolon obtained. No methyl quinazolon could be found although the experiment was repeated several times and the by-products carefully examined.

Properties.

The ethyl quinazolon obtained by the above methods agreed in all its properties with those observed by Bischler and Lang¹ and by Niementowski.² It crystallizes from water in long fine needles which are moderately soluble in hot water, slightly in cold, easily in alcohol and benzene. Its melting-point is given by Bischler and Lang as 227°-228° and by Niementowski as 225°. The writer found 227°-228° to be the uncorrected melting-point and 234° the corrected.

Derivatives.

Methyl Ether, C₆H₅N=C-C₂H₅.—This is prepared by

heating the quinazolon with caustic alkali and methyl iodide in alcoholic solution, for a few hours, with a return condenser, evaporating the alcohol and treating the residue with water. Sometimes the addition of a little more caustic alkali is necessary at this point to cause the complete separation of the ether, which is then filtered out and crystallized from water. It forms long colorless needles melting at 121°.

Hydrochloride.—This salt results from the action of hydrochloric acid on the quinazolon. It crystallizes in needles which sublime without melting.

Nitrate.—The nitrate crystallizes from a hot solution of the base in nitric acid (1 : 4) in the form of coarse yellow needles which melt with decomposition at 173°-174°.

Sulphate.—This salt is obtained by saturating cold dilute sulphuric acid with quinazolon, filtering and concentrating the filtrate. It forms coarse needles which gradually darken on heating and melt at 240°-241°.

Chromate.—The chromate crystallizes from a hot concentrated aqueous solution of quinazolon and chromic acid, in the form of light brown needles which decompose at about 155°.

Picrate.—This is prepared in the same way as the chromate but is less soluble in cold water. It crystallizes in thin plates of a light yellow color and melts at 191°-192°.

¹ *Ber. d. chem. Ges.*, 28, 280.

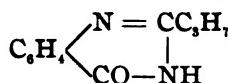
² *J. prakt. Chem.*, (2), 51, 564.

Oxalate.—This is also prepared as is the chromate and forms long needles melting at 180–181°.

Chlorplatinate.—The quinazolon is dissolved in hot hydrochloric acid and an excess of platinic chloride added; on cooling, the double salt separates as a red crystalline powder. It was analyzed for platinum with the following results:

	Calculated for (C ₁₀ H ₁₀ N ₂ O.HCl) ₂ PtCl ₆ .	Found.
	I.	II.
Platinum.....	25.63	25.66 25.63

2-n-PROPYL 4-KETODIHYDROQUINAZOLIN.



Preparation.

I. *Anthrаниlic Acid and n-Butyronitrile.*—The tube was heated to 120°–125° for four and one-half hours, 200°–210° for six hours, and 210°–220° for six hours, opening after each period. The pressure was considerable only after the second period and the product was crystalline. After the usual sodium carbonate treatment the residue was crystallized from water. The quinazolon thus obtained was dissolved in cold caustic alkali to separate it from *n*-butyranilide but none of the latter was found. The base was then precipitated with carbon dioxide as usual and crystallized from water. The yield was about 17 per cent.

The sodium carbonate solution used in the first treatment was evaporated, the residue extracted with ether, and the extract crystallized from benzene. Leaflets were obtained melting at 112°–113°, very soluble in water, and evolving ammonia when boiled with caustic alkali. Hofmann¹ states that *n*-butyramide melts at 115°.

II. *Anthrаниlic Acid, n-Butyronitrile, and n-Butyric Anhydride.*—A tube containing these substances was heated to 180°–190° for four hours and to 190°–200° for five hours. The yield was 30 per cent. Another tube heated to 180°–190° for five and one-half hours and to 210°–220° for six hours gave 39 per cent.

There was practically no pressure in either case and the contents were very light-colored. Both products were treated in the same way; first washed with sodium carbonate solution and then twice crystallized from water, decolorizing with bone-black.

¹ *Ber. d. chem. Ges.*, 15, 982.

The soda solutions were found to contain *n*-butyramide as in the last case.

No butyranilide was found and none was expected from the fact that the slight pressure in the tubes showed that practically no anthranilic acid had decomposed.

III. Anthranilic Acid, Acetonitrile, and *n*-Butyric Anhydride.—The tube was heated to 180°–190° for five hours and to 210°–220° for six hours. There was no pressure. The contents were treated as in (II). The quinazolon obtained agreed in all its properties with *n*-propylquinazolon. The yield was about 28 per cent.

By evaporating the soda solution, extracting the residue with ether, and crystallizing the extract from benzene, a very small amount of material was obtained which softened at 93°, but was not entirely melted at 130°. It dissolved completely in cold dilute caustic potash and was reobtained by passing carbon dioxide and concentrating the solution. On crystallizing from benzene it now melted at 232°–233° (uncorrected), and was probably methyl quinazolon.

IV. Anthranilic Acid, *n*-Butyronitrile, and *n*-Butyric Acid.—The tube was heated for three periods of six hours each to 165°–175°, 210°–215°, and 230°–240°. After each of the first two periods there was considerable pressure, but after the third, there was none. The product was treated successively with soda solution and dilute caustic alkali, and the quinazolon precipitated from the latter solution as usual by passing carbon dioxide. It was purified by crystallization from water.

The part insoluble in the caustic alkali was found, on recrystallizing from dilute alcohol, to be *n*-butyranilide. It melted at 93°–94° and yielded aniline when boiled with concentrated alkali. Gerhardt¹ gives the melting-point of *n*-butyranilide as 90° but the writer found that anilide prepared by boiling *n*-butyric acid with aniline for a few hours, pouring the product into water, and crystallizing the precipitate from dilute alcohol, melted at 93°–94°, and otherwise agreed with that obtained from the tube.

The soda solution, as usual, contained *n*-butyramide.

Properties.

Normal propyl quinazolon has been prepared by Bischler and Lang,² who found the melting-point to be 205°. While in all

¹ *Ann. Chem. (Liebig)*, 87, 166.

² *Ber. d. chem. Ges.*, 28, 286.

other properties the quinazolon obtained by the writer agrees with that of these authors, its melting-point is 199° - 200° .

Derivatives.

The salts and ethers of this and the following quinazolons were almost all prepared in exactly the same way as were those of ethyl quinazolon and therefore only their properties are given.

Methyl ether, $C_6H_4\begin{cases} N = C - C_3H_7 \\ | \\ CO - N - CH_3 \end{cases}$, crystallizes from water in

long colorless needles melting at 77° - 78° .

Hydrochloride.—Thin plates which sublime without melting.

Nitrate.—Coarse flat needles melting with decomposition at 159° - 160° .

Sulphate.—Long coarse needles melting at 227° - 228° :

Chromate.—Yellow crystalline powder. On heating, it gradually darkens, commencing at about 150° .

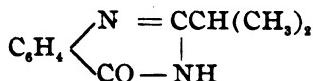
Picrate.—Light yellow needles with serrated edges, melting at 183° - 184° .

Oxalate.—White needles melting at 193° - 194° .

Chlorplatinate.—Coarse red crystals. The platinum was determined by ignition.

	$(C_{11}H_{12}N_2O.HCl)_2PtCl_4$	Calculated for		Found.
		I.	II.	
Platinum.....	24.71	24.79	24.82	

2-ISOPROPYL 4-KETODIHYDROQUINAZOLIN.



No isobutyric nitrile being conveniently at hand, its action alone on anthranilic acid could not be studied. It was found, however, that, for the production of isopropyl quinazolon, the use of isobutyric nitrile was unnecessary, and that the combined action of isobutyric anhydride and a lower nitrile, acetic or propionic, on anthranilic acid resulted in its formation, the yield, especially with propionitrile, being very good.

I. *Anthranilic Acid, Isobutyric Anhydride, and Propionitrile*.—The tube was heated to 180° - 190° for five hours, 210° - 220° for five hours, and 230° - 240° for twelve hours. The pressure at any time was very slight. After preliminary treatment with sodium

carbonate solution the product was crystallized from alcohol and decolorized with bone-black. The yield of quinazolon was about 40 per cent.

Another tube was heated to 180° - 190° for six hours and to 210° for six hours and yielded 32 per cent.

No trace of ethyl quinazolon was found in either of these tubes.

II. Anthranilic Acid, Isobutyric Anhydride, and Acetonitrile.—This tube was heated to 180° - 190° for five hours and 210° - 220° for six hours and yielded 15½ per cent. of isopropyl quinazolon, the process of purification being the same as when using propionitrile.

Properties.

Bischler and Lang¹ and Niementowski² have prepared isopropyl quinazolon but differ as to its melting-point, the former giving it as 195° - 196° and the latter as 224° . Niementowski³ has suggested that this difference may be due to a difference in constitution in the sense of tautomerism.

The quinazolon obtained by the writer melts at 225° - 226° uncorrected or at 231° - 232° corrected; it therefore agrees quite well with Niementowski's product. Its other properties are the same as those recorded by these authors.

A peculiarity in the solubility of this base was observed by the writer, which possibly indicates that it consists of a mixture of the two forms, keto and hydroxy? While all the other quinazolons, when in a fluffy crystalline condition, dissolved instantly in cold dilute caustic alkali, it was found that the isopropyl showed a difference in the rapidity of solution. Only a portion dissolved instantly; the rest remained undissolved for a short time, though it ultimately also went into solution. In one case the slower dissolving portion was filtered out, washed, and dried. Its melting-point was found to be 223° , while the portion which had dissolved, when precipitated with carbon dioxide and crystallized from alcohol, melted at 231° - 232° , the ordinary melting-point of the quinazolon. No further work has, at present, been done on this subject.

¹ *Ber. d chem. Ges.*, 28, 287.

² *J. prakt. Chem.* (2), 51, 569.

³ *Ber. d. chem. Ges.*, 27, R., 516.

Derivatives.

Methyl Ether, $C_6H_4\begin{cases} N = C - C_3H_7 \\ | \\ CO - N - CH_3 \end{cases}$.—Long silky needles melting at 78° – 79° .

Hydrochloride.—Rectangular plates.

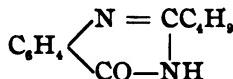
Sulphate.—Coarse needles melting at 219° – 220° .

Chromate.—Transparent coarse brown needles which decompose on heating.

Pierate.—Light yellow crystalline powder melting at 213° – 214° .

Chlorplatinate.—Coarse red crystals. The platinum was determined by ignition.

	Calculated for $(C_{11}H_{12}N_2O \cdot HCl)_2PtCl_4$	Found.
	I.	II.
Platinum.....	24.71	24.85 24.69

2-ISOBUTYL 4-KETODIHYDROQUINAZOLIN.*Preparation.*

I. *Anthranilic Acid and Isovaleronitrile*.—The tube was heated to 160° – 165° for five hours and to 200° – 210° for five hours. Moderate pressure was found on opening, and the contents were dark-colored but crystalline. They were heated with dilute caustic potash solution for a short time, the solution cooled, filtered, and carbon dioxide passed into the filtrate. The precipitated quinazolon was then crystallized from water. The yield was only 5 per cent. of the theoretical.

II. *Anthranilic Acid, Isovaleronitrile, and Isovaleric Anhydride*.—The mixture was heated successively to 180° – 190° for five hours, 210° – 220° for five hours, and 230° – 240° for twelve hours. The pressure in the tube was very slight and the contents were light-colored and entirely crystalline. They were treated with soda solution and then crystallized from dilute alcohol. To separate the quinazolon from isovaleranilide the treatment with cold dilute caustic alkali was applied to this product. The anilide was crystallized from dilute alcohol and obtained in the form of colorless needles melting at 112° – 113° , and yielding aniline when boiled with concentrated alkali. The quinazolon, after precipita-

tion with carbon dioxide, was crystallized from water and amounted to 35 per cent. of the theoretical yield.

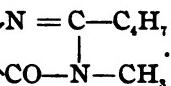
The soda solution with which the tube-contents were first treated was evaporated and the residue extracted with ether. The extract was crystallized from benzene and found to be isovaleramide melting at 131° , and evolving ammonia when boiled with alkali.

Another tube containing the same materials and heated to 190° - 200° for three hours and to 225° for six hours yielded 26 per cent.

Properties.

Isobutyl quinazolon crystallizes from water in small needles melting at 194° - 195° . It is moderately soluble in hot water, very slightly in cold, somewhat in ether, and easily soluble in alcohol and hot benzene.

Derivatives.

Methyl Ether, C_6H_4  Colorless needles melting at 68° - 69° .

Hydrochloride.—Coarse needles.

Nitrate.—Yellow plates decomposing at 171° - 172° .

Sulphate.—Needles arranged in bunches and melting at 228° - 229° .

Chromate.—Yellow crystalline powder which decomposes at 154° .

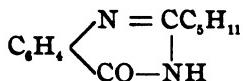
Picrate.—Light yellow needles melting at 192° .

Oxalate.—White felted needles melting at 204° - 205° .

Chlorplatinate.—Transparent coarse brown needles. It was analyzed for platinum.

	Calculated for $(C_{12}H_11N_2O.HCl)_2PtCl_4$	Found. I. II.
Platinum.....	23.86	23.93 24.00

2-ISOAMYL 4-KETODIHYDROQUINAZOLIN.



Preparation.

I. *Anthranilic Acid and Isocapronitrile*.—The tube was heated to 180 - 185° for five hours, to 220 - 225° for six hours, and to 240 -

250° for six hours. Moderate pressure was found after the first period but none after the second and third. The quinazolon was extracted and purified exactly as was isobutyl quinazolon (I). The yield was 18 per cent.

II. *Anthranilic Acid, Isocapronitrile, and Isocaproic Acid.*—This tube was heated successively to 185°–190°, 210°–215°, and 230°–240° for six hours each. Considerable pressure was found only after the first heating. The product was treated in exactly the same way as was that of the isobutyl tubes (II). The yield of quinazolon was 37 per cent.

An anilide was found as usual. It crystallized from dilute alcohol in long needles melting at 110°–111°, and yielding aniline when boiled with alkali.

0.1533 gram gave 9.9 cc. nitrogen (20°, 761 mm.).

	Calculated for $C_{12}H_{17}NO.$	Found.
Nitrogen.....	7.33	7.39

It is therefore, as was expected, isocaproanilide. As the properties of this anilide have apparently not been recorded, some was prepared by boiling isocaproic acid with aniline for a short time, pouring the product into water, and crystallizing the precipitate from dilute alcohol. Its properties were found identical with those of the anilide obtained from the tube.

0.1814 gram gave 11.9 cc. nitrogen (21°, 762 mm.).

	Calculated for $C_{12}H_{17}NO.$	Found.
Nitrogen.....	7.33	7.49

Another by-product found in this tube was isocaproamide, extracted from the sodium carbonate solution by the usual method. It melted at 119°–120° and evolved ammonia when boiled with alkali.

Properties.

Isoamyl quinazolon crystallizes from water in very small felted needles melting at 184°. It is soluble in ether, alcohol, and benzene, moderately in boiling water and almost insoluble in cold. The nitrogen was determined with the following results:

I. 0.1563 gram gave 18.3 cc. nitrogen (23°, 752 mm.).

II. 0.1494 gram gave 17.3 cc. nitrogen (22°, 753 mm.).

	Calculated for $C_{12}H_{16}N_2O.$	Found.
	I.	II.
Nitrogen.....	12.96	13.05 13.02

Derivatives.

Methyl Ether, $C_6H_5\begin{array}{c} N = C - C_6H_{11} \\ | \\ CO - N - CH_3 \end{array}$.—This ether is more

difficult to obtain crystalline than is that of any of the other quinazolins. It was prepared in the usual way by heating the quinazolon with methyl iodide and caustic alkali in alcoholic solution. The alcohol was evaporated, the residue taken up with water, and extracted with ether. The ether solution was evaporated and the methyl ether obtained in the form of an oil, which solidified only after long standing in a desiccator. To obtain it in crystals various solvents were tried, but without success. The method finally used was to form the hydrochloric acid salt, dissolve it in water, add a slight excess of sodium carbonate, while cooling with ice, and finally inoculating the milky solution with some of the solid ether obtained in the desiccator. On standing, crystals finally appeared in the form of small needles melting at 40° - 41° , and practically insoluble in water.

Hydrochloride.—Fine needles.

Nitrate.—Thin plates decomposing at 160° - 161° .

Chromate.—Attempts to prepare this salt were unsuccessful. The methods used were the action of chromic acid on the base and double decomposition between the hydrochloride of the base, and potassium chromate. In neither case was any crystalline product obtained, the base apparently decomposing.

Picrate.—Yellow leaflets melting at 164° - 165° .

Chlorplatinate.—This salt could not be obtained, the affinity between the hydrochloride of the base and platinic chloride seeming to be very weak.

In general it appears that the salts of the higher quinazolons are weaker and more easily dissociated than are those of the lower.

MISCELLANEOUS REACTIONS.¹*Nitrile and a Lower Acid Anhydride.*

I. *Anthranilic Acid, Propionitrile, and Acetic Anhydride*.—The tube was heated to 140° - 150° for three hours, 180° - 190° for five hours, and 200° - 205° for six hours. There was practically no

¹ The order and numbering of these reactions are the same as in the first part of the paper.

pressure at any time and the contents were completely crystalline. After washing with sodium carbonate solution, the product was extracted with boiling water. From this solution, on cooling, methyl quinazolon separated in considerable quantity. The residue, after the water extraction, was a brown amorphous powder from which nothing crystalline could be obtained.

The methyl quinazolon was identified by its melting-point, physical properties, and by the melting-point of its methyl ether.

No ethyl quinazolon was found.

II. *Anthranilic Acid, Isocapronitrile, and Isobutyric Anhydride.*

—The mixture was heated to 210° – 220° for five and one-half hours. The pressure, on opening, was slight and the contents were light-colored and crystalline. After preliminary treatment with sodium carbonate, the caustic alkali method of extraction was applied to the residue.

The quinazolon so obtained melted gradually from 200° – 205° , and, when sublimed, these limits were increased to 180° – 210° , while the melting-points of the two possible products, isopropyl and isoamyl quinazolons are, respectively, 225° – 226° and 179° – 180° (uncorrected). Recrystallization three times from water did not appreciably change this point. Three crystallizations from alcohol were necessary to obtain pure isopropyl quinazolon melting at 226° – 227° (uncorrected). A system of fractional crystallization was applied to the mother-liquor but no product was obtained melting wholly below 205° , although several began to melt around 190° .

That this product and those obtained from some of the reactions still to be described are mixtures seems certain when it is considered that in all other cases the quinazolons were obtained pure after the caustic alkali treatment and one crystallization, and that, as the reactions proceeded just as smoothly, it is unlikely that any exceptional impurities were formed. The difficulty in separating the mixtures is due to the great similarity in the properties of their constituents; the successful identification of isopropyl quinazolon in the reaction just described is due to its slightly smaller solubility in alcohol as compared with isoamyl quinazolon; it was also undoubtedly present in the larger quantity.

III. *Anthranilic Acid, Isocapronitrile, and n-Butyric Anhydride.*

—Heated to 180° – 185° for five hours, 220° – 225° for six hours, and

240°-250° for six hours. The pressure was very slight at any time and the contents crystalline. The soda and caustic alkali method of purification was used. The quinazolon obtained melted at 187°-188°, and, on recrystallization, at 184°-187°. The two quinazolons which it was possible to have formed in this reaction, the normal propyl and the isoamyl, melt respectively at 194°-195° and 179°-180° (uncorrected).

As the methyl ether of the normal propyl quinazolon is quite soluble in hot water while that of the isoamyl is almost insoluble, it was thought that this might prove a method of separation. Only the ether of normal propyl quinazolon could, however, be identified; but, on account of the small amount of material available and the difficulty experienced in getting isoamyl quinazolon methyl ether crystalline, as already mentioned, this can hardly be considered a proof that none of that base was present.

Nitrile and a Higher Acid.

I. *Anthranilic Acid, Acetonitrile, and Propionic Acid.*—The tube was heated to 170°-180° for five hours. On opening, a moderate pressure was observed. The contents were treated exactly as in the last reaction. The quinazolon obtained melted at 213°-214° (uncorrected), and this point remained constant on sublimation. Recrystallization from water raised it to 218°-220°, and this also did not change on sublimation. Methyl and ethyl quinazolons melt, respectively, at 232° and 227°-228° (uncorrected), while their methyl ethers melt at 110°-111° and 121°-122° (uncorrected). The methyl ether obtained from the supposed mixture melted indefinitely at from 90°-105°.

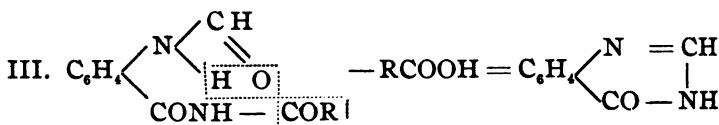
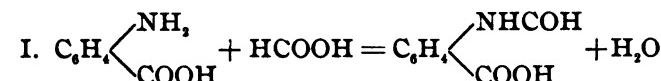
II. *Anthranilic Acid, n-Butyronitrile, and Capric Acid.*—The mixture was heated to 185° for six hours and to 200°-210° for five and one-half hours. The pressure was moderate and the tube-contents light in color and crystalline. The quinazolon was separated and purified as in the last case and was found to be the pure normal propyl derivative melting at 199°.

III. *Anthranilic Acid, Isocapronitrile, and Capric Acid.*—The tube was heated exactly as was No. 2. After the first period the pressure was moderate and the contents consisted almost entirely of a dark red liquid with a very small amount of solid matter; after the second period, however, they were wholly crystalline. By following the same method of separation as in No. 2 and crys-

tallizing the product from dilute alcohol, pure isoamyl quinazolon, melting at 184° , was obtained.

Nitrile and a Lower Acid.

The following experiments of heating anthranilic acid with formic acid and various nitriles were performed in the hope of obtaining 4-ketodihydroquinazolin itself, as follows :



In the other experiments on the action of acids and nitriles on anthranilic acid it was found that, apparently, the question as to whether a single or a mixture of quinazolons will form depends on the ease with which the fatty acid combines with the anthranilic acid to form an acylantranilic acid; it was thought, therefore, that, as formic and anthranilic acids react with the greatest ease, the above reaction was a very likely one. On trial, however, it was found that while formylantranilic acid is quickly formed it apparently does not react with nitriles at temperatures at which it is stable; according to Meyer and Bellmann,¹ formylantranilic acid, when heated with water, decomposes at $130^{\circ}-140^{\circ}$ into formic acid, carbon dioxide, and aniline.

I. Anthranilic Acid, Formic Acid, and Acetonitrile.—One tube containing these was heated to $100^{\circ}-110^{\circ}$ for twelve hours. There was no pressure and the contents were completely crystalline. On adding sodium carbonate solution the entire product dissolved, showing that no quinazolon was present. The addition of hydrochloric acid to the solution caused a precipitate, which, washed and crystallized from water, was found to be formylantranilic acid, melting at $165^{\circ}-166^{\circ}$.

Another tube was heated to 100° , $140^{\circ}-150^{\circ}$, and $190^{\circ}-200^{\circ}$ for six hours each. After the first period there was no pressure and

¹ *J. prakt. Chem.*, (2), 33, 25.

the contents were crystalline and much as in the first tube; after the second, the pressure was moderate and the contents were entirely liquid; after the third, there was again moderate pressure and the contents consisted of about half crystals and half liquid. The treatment with sodium carbonate followed by dilute caustic alkali was applied, but, on passing carbon dioxide into the alkali solution, the precipitate obtained was so slight that nothing further was done with it.

II. Anthranilic Acid, Formic Acid, and Propionitrile.—The results from this reaction were as unsatisfactory as those just detailed.

III. Anthranilic Acid, Formic Acid, and Isocapronitrile.—This tube was heated to 120° – 125° for five hours, 160° – 170° for six hours, and 210° – 220° for six hours. There was considerable pressure and the product consisted of a sirupy liquid and a small amount of crystalline material. The same treatment as in the previous tubes was used and a small amount of isoamyl quinazolon obtained.

The sodium carbonate solution was evaporated, the residue extracted with ether, and the extract crystallized from benzene. Two kinds of crystals were obtained and these were separated by treatment with warm benzene, which dissolved one faster than the other. The more soluble substance was found to be isocaproamide, melting at 119° – 120° , while the less soluble one, melting at 190° – 195° , and, on sublimation, at 211° (uncorrected), was probably 4-ketodihydroquinazolin. The melting-point of this quinazolon is stated by Knape¹ to be 211° – 212° and by Bischler and Burkart² to be 209° .

As it has been shown that the best yields of quinazolon were obtained when using the nitrile and the corresponding acid or anhydride, the correct nitrile to use with formic acid, for the production of 4-ketodihydroquinazolin, is formic nitrile or hydrocyanic acid. No anhydrous hydrocyanic acid being available, a few experiments were tried aiming to produce the acid in the tube as the reaction proceeded, but no encouraging results were obtained.

IV. Anthranilic Acid, Isocapronitrile, and Propionic Acid.—The mixture was heated to 170° – 180° for five hours and then to 200° –

¹ *J. prakt. Chem.*, (2), 43, 214.

² *Ber. d. chem. Ges.*, 26, 1349.

210° for six hours. There was considerable pressure after the first period but none after the second. The contents were almost wholly crystalline. The quinazolon was extracted and purified by the same method as followed above, and proved to be the isoamyl derivative. Its melting-point was 183° - 184° .

Action of Fatty Acids and Anhydrides on Anthranilic Acid.

These experiments were performed for the purpose already stated on page 614. Anthranilic acid was heated with normal butyric and isocaproic acids respectively, both in sealed tubes and open, at temperatures varying from but slightly above 100° to the boiling-point of the fatty acid, without any action being discernible. In contradistinction to this it was found that both normal butyric and isovaleric anhydrides reacted quite smoothly to form the corresponding acylantranilic acids. Merely heating the acid and anhydride together on the water-bath for three to four hours was sufficient to give a yield of about 30 per cent.

Only the isovalerylantranilic acid was closely examined. It crystallizes from water in needles melting at 110° - 111° .

I. 0.1816 gram gave 10.6 cc. nitrogen (26° , 755 mm.).

II. 0.2016 gram gave 11.7 cc. nitrogen (23° , 754 mm.).

	Calculated for $C_{12}H_{16}NO_2$	Found.	
	I. II.	I. II.	II.
Nitrogen.....	6.33	6.43	6.49

This work is being continued and extended, and other papers will appear shortly.

ORGANIC LABORATORY, HAVEMAYER HALL,
COLUMBIA UNIVERSITY, June 1, 1901.

ON THE ESTIMATION OF UREA IN URINE.

BY J. H. LONG.

Received July 23, 1901.

Inasmuch as about 90 per cent. of the total assimilated nitrogen leaving the human body is excreted in the form of urea the accurate determination of this substance in the urine must remain among the most important of physiological-chemical problems. The interest attaching to the question is fully shown by the great number of contributions to the subject appearing in the chemical literature, yet, notwithstanding all that has been written, the problem is still far from satisfactory solution. In the older text-books of urine analysis the Liebig method by use of mercuric

nitrate held long the first place, which was later taken by that of Knop and Hüfner, depending on the reaction between a hypochlorite or hypobromite and urea.

The original Liebig method was found to give results which were too high because of the precipitation of other substances than urea by the mercuric nitrate, and as the extent of the possible error here became more and more apparent, the method fell into disfavor and was finally practically discarded. In the later editions of the well-known manual of urine analysis by Neubauer and Vogel, revised by Huppert, the Liebig process is no longer described among the quantitative methods.

The fate of the hypobromite processes, as scientific methods, is almost as interesting. In these, plus and minus errors were long supposed to nearly balance each other. A part of the urea fails to decompose according to the simple reaction,



while, on the other hand, many other nitrogenous bodies in the urine give up a large but variable part of their nitrogen in the free form under the influence of the same reagent. The modifications of this general method are almost beyond number, but in the final results there is probably even less constancy than in the older mercury method. In the editions of the Neubauer and Vogel work referred to above the Knop-Hüfner method is described only among the qualitative reactions.

From the standpoint of those interested in the practical determination of urea this omission must be looked upon as a mistake since the supposedly more accurate processes which are now described are not at all suited for quick comparative determinations in cases where many tests have to be made. It is possible that the mercury method, under special circumstances, may still render service here, and it is the object of this communication to point out how certain corrections may be applied, where comparatively full analyses are being made, with fresh urine.

The main sources of error in titrations of urea in urine by the standard solution of mercuric nitrate are these :

a. The chloride present retards the reaction, but as this effect has long been accurately known and easily corrected it will not be discussed in this place.

b. Ammonia which is always normally present, even in fresh

urine, combines likewise with the mercury solution, and prevents precipitation until a certain excess of the latter is added.

c. Uric acid, which amounts to 800 mg., or more sometimes, in the day's urine combines with the reagent to form a definite compound. The effect of this is, however, relatively small.

d. Creatinin, after urea the most abundant of the nitrogenous urinary products, forms several crystalline combinations with mercuric nitrate. The composition of these is variable with the concentration of the reacting solutions, but in any event the error in the titration of the urea in presence of this body is quite appreciable.

e. In addition to the above, several other nitrogenous compounds, present in small amount in the urine, are known to combine with mercuric nitrate, but their effect is extremely small and may usually be neglected.

I have undertaken to estimate the effect of the main disturbing factors referred to and present below some experimental data.

AMMONIA.

In fresh normal urine the amount of ammonia present is about 600 mg. for each 1000 cc. of excretion. In urine which is allowed to stand, the amount rapidly increases from decomposition of the urea. To determine the influence of this small weight of ammonia in urea titrations, tests were carried out on solutions containing ammonia alone, in the form of nitrate, and on solutions containing ammonia and urea. The ammonia was used in the form of nitrate because in the usual method of preparing urine for titration it would be left in that combination.

Experiment 1.—A solution was made which contained in 500 cc. 2.5 grams of pure ammonium nitrate. This corresponds to 1.06 gram of NH₃ to the liter; 20 cc. of this solution were measured into a beaker and standard mercuric nitrate solution added. No precipitate appeared but at the same time no reaction immediately followed on bringing a drop of the liquid in the beaker in contact with a paste of sodium bicarbonate and water. It was found that about 2.5 cc. of the usual standard mercuric nitrate solution must be used before a reaction appeared, indicating the presence of an excess of the mercury. Neutralization of the liquid in the beaker with sodium carbonate made no appreciable difference in the result.

Experiment 2.—Tests were made with a weaker ammonia solution containing 0.6 gram to the liter. The results were nearly the same as before, the volume of the mercury solution required being, however, relatively a little greater. As the end reaction is by no means as sharp as with pure urea solutions it is easy to pass the right end-point in titration. Many single titrations were made and as a mean of the closely agreeing results it may be said that with the solutions used, 20 mg. NH_3 = 2.5 cc. of the mercury solution.

This corresponds to 17 NH_3 , to 2.12 cc. mercury solution, 17 NH_3 , to 164 mg. HgO , 1 mol. NH_3 , to 0.75 mol. HgO , or 4 NH_3 , to 3 HgO , approximately.

Experiment 3.—Here solutions containing both urea and ammonia were titrated. The urea solution used contained exactly 2 grams in 100 cc. In a series of experiments it was found that mixtures containing 10 cc. of this urea solution, and 10 cc. of the first described ammonia solution required 21.6 cc. of the mercury solution instead of 20 cc. This makes the effect of the ammonia a little greater than in the above experiments, 1 and 2. But as intimated, the reaction is not as clear as in absence of ammonia, and a trifling excess must always be added from the mercuric nitrate burette. The end-point seems to vary also slightly with the temperature.

As a mean result the presence of 10 mg. of ammonia in the 20 cc. of mixed liquid titrated increases the amount of mercury solution used by about 1.6 cc. This corresponds closely to 1 cc. of the mercury solution for 6 mg. of ammonia, and this is the average amount present in 10 cc. of urine, the volume usually taken for titration; this is much lower than is a result given by Feder¹ according to whom 10 mg. of ammonia require 2.6 cc. of the mercury solution. This result is probably too high, and was not approached in any one of the numerous single titrations I made.

URIC ACID.

The amount of uric acid in the urine was formerly much underestimated, but since the introduction of better methods of determination higher, and probably pretty accurate, results may be easily obtained. In a large number of urines studied in this laboratory, the uric acid has been found to amount to about 650 mg.

¹ See Neubauer and Vogel: "Urine Analysis," 8th German Edition, p. 272.

for 1000 cc. of urine. In 10 cc. of urine we have therefore about 6.5 mg. of uric acid normally, and it is the interference of this that we have to consider in the urea titration. For the experiments I made up a test solution containing 250 mg. of pure uric acid dissolved by the aid of a little alkali to make 250 cc. The behavior of this with the mercury solution is regular and the same slight increase is found whether we use the simple uric acid solution or one containing uric acid and urea.

For a solution containing in 20 cc. 200 mg. of urea, and 5 mg. of uric acid the amount of mercury solution required was just 0.1 cc. more than for the urea solution alone, and by increasing the uric acid the increase in the required mercuric nitrate was found to be in the same proportion. The correction for the presence of uric acid is therefore very small, and in any case would not exceed 0.15 cc. of the mercury solution for the volume of 10 cc. of urine ordinarily taken for the titration.

CREATININ.

This is present in urine to the extent of 1 gram to 1.6 grams or more in the volume of 1000 cc. In a large number of tests I found an average of 1.4 grams by the method of precipitation with zinc chloride. On this basis 10 cc. of urine would contain 14 mg. of creatinin.

To study the behavior of this body I first prepared it in pure condition from urine by decomposing the zinc chloride precipitate with lead hydroxide. Later much larger quantities were made by separating first pure creatin from extract of beef and then decomposing the product obtained by long heating of this with strong hydrochloric or 25 per cent. sulphuric acid, by means of lead hydroxide or barium carbonate.

As was long ago pointed out by Neubauer¹ mercuric nitrate added to a creatinin solution produces no immediate precipitate; a combination is formed in which acid is liberated and this interferes with precipitation. On neutralizing the liquid with sodium carbonate a point is reached, however, when a precipitate soon forms and settles out. Under certain conditions a precipitate with the composition $(C_4H_7N_3O)_2Hg(NO_3)_2HgO$ may be obtained in this way. But with variations in the concentration of the reacting bodies the composition of the precipitate varies, as I have found by experiment. In the titration of weak creatinin solutions

¹ See Neubauer and Vogel: "Urine Analysis."

similar results are found ; the solution must be neutralized with sodium carbonate to secure precipitation. In tests made I employed a creatinin solution containing 1 gram in 100 cc.

Experiment 1.—Of this solution I took 10 cc. and added nearly 5 cc. of the mercuric nitrate solution before any appreciable reaction appeared, on testing as usual with sodium bicarbonate. The solution in the beaker was still quite clear ; a little methyl orange was added and then 3 cc. of normal sodium carbonate solution to change of color. This is a rough measure of the liberated acid.

Experiment 2.—In a second experiment with 20 cc. of the creatinin solution, 9 cc. of the mercuric nitrate were added before securing a trace of a reaction in the sodium bicarbonate. With 10 cc. of the mercury solution the reaction was sharp and 1 cc. of normal sodium carbonate was added to produce haziness in the liquid in the beaker. It appears, therefore, that about 9.5 cc. of the standard mercuric nitrate solution may be taken as equivalent to 20 cc. of the creatinin solution. For this concentration this corresponds very closely to a relation of 1 molecule of creatinin to 2 molecules of mercuric oxide. The experiments were many times repeated.

Experiment 3.—Numerous tests were made with weaker creatinin solutions containing amounts corresponding with those in urine. Here the volume of mercury solution used was always relatively a little greater, suggesting a combination of 1 molecule of creatinin with $2\frac{1}{2}$ molecules of mercuric oxide, but the difference is doubtless due mainly to the slight excess required to give a reaction in dilute solution.

Experiment 4.—In titrating mixtures of urea and creatinin the same general difference was found as last shown, the reaction with urea being apparently slightly retarded by the presence of the creatinin. Tests of mixtures were made in large number so that the result may be looked upon as well established.

The final value of all these reactions may then be expressed as follows, the corrections being those necessary for average normal urine :

6 mg. NH ₃	in 20 cc. (10 cc. urine, 10 cc. water)	require 1.0 cc. Hg sol.
7.5 " C ₆ H ₄ N ₄ O ₃ " 20 "	10 " " 10 " " " 0.15 " " "	
14.0 " C ₆ H ₄ N ₃ O " 20 "	10 " " 10 " " " 0.85 " " "	
		2.00

The average correction to be made then on the Liebig titration is 2 cc. of the mercuric solution, but as readily seen this can be applied to fresh urine only since in old urine the effect of the ammonia of decomposition becomes too great to be easily corrected. In the clinical examination of fresh urine the correction may be applied with only a small margin of error, while in fuller analyses, where the disturbing factors are also estimated, it may be used with considerable accuracy. My thanks are due to Mr. Grulee, who made many of the experiments above.

NORTHWESTERN UNIVERSITY, CHICAGO,
July 20, 1901.

ON THE DETERMINATION OF FORMALDEHYDE.

BY A. G. CRAIG.

Received July 20, 1901.

THE methods for the determination of formaldehyde may be classed, by their reactions, in three groups, as follows:

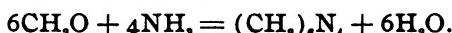
Group 1.—Depending on a specific reaction.

Group 2.—Formation of addition products with elimination of the elements of water.

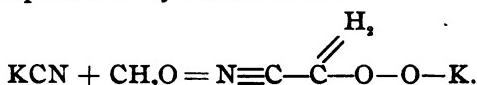
Group 3.—Oxidation and reduction.

Group 1 contains:

(a) The ammonia method.¹



(b) The potassium cyanide method.²

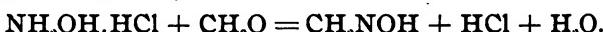


(c) The fixed alkali method.³

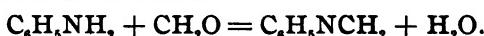


Group 2 contains:

(a) The hydroxylamine method.⁴



(b) The aniline method.⁵



The precipitate is weighed.

¹ L. Legler: *Ber. d. chem. Ges.*, 16, 1333.

² G. Romijn: *Ztschr. anal. Chem.*, 36, 18.

³ Legler: *Ber. d. chem. Ges.*, 16, 1333.

⁴ Brochet and Cambier: *Compt. rend.*, 120, 449.

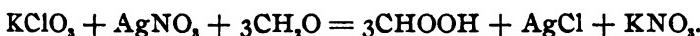
⁵ Trillat: *Bull. Soc. Chim.*, [3], 9, 305.

(c) Same as above except that the excess is titrated.¹

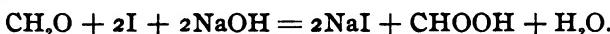
Group 3 contains most of the methods which have been proposed.

(a) The ammoniacal silver nitrate method² depends on the reduction of metallic silver when silver nitrate is boiled with ammonia and formaldehyde.

(b) The acid silver nitrate method.³



(c) The iodine method.⁴



(d) The alkaline permanganate method.⁵

(e) Another potassium permanganate method.⁶

(f) The bichromate method.⁷

(g) The hydrogen peroxide method.⁸



A careful study of the various methods and the comments on them brought out the fact that no fixed standard had been used to test the accuracy of the methods, but that the highest or the average results were taken to be the best.

A sample of trioxymethylene was prepared by evaporation. Trials were made of titration with potassium permanganate and oxalic acid. The end-point was sharp, and tests showed that the formaldehyde was completely destroyed.

The most successful scheme was as follows: 280 cc. bottles, having glass stoppers closed with graphite and tied down; trioxymethylene, about 0.5 gram.; 25 cc. 1:1 sulphuric acid; 40 cc. 1 per cent. potassium permanganate. The bottle is closed and heated to 80° C. for fifteen minutes. The solution is then cleared up with standard oxalic acid and titrated to pink. The results obtained were 96.4 per cent. and 96.0 per cent.

A trial was made of sealing some of the sample in a test-tube with water and heating. Solution was complete in one-half hour at 100° C. The results by titration were unsatisfactory. Fear-

¹ Klar: *Pharm. Ztg.*, **40**, 611.

² Orchard: *Analyst*, **22**, 4.

³ Grützner: *Arch. Pharm.*, **234**, 634.

⁴ G. Romijn: *Ztschr. anal. Chem.*, **36**, 18.

⁵ Smith: *Analyst*, **21**, 148.

⁶ Jones: *Am. Chem. J.*, **17**, 539.

⁷ Nicloux: *Bull. Soc. Chim.*, [3], **17**, 839.

⁸ Blank and Finkenbeiner: *Ber. d. chem. Ges.*, **31**, 2979.

ing that the sample might be impure, some of it was sublimed in a combustion tube tightly closed, with a cannon tube at one end and a condenser at the other. The pressure did not rise very high. The sublimate collected in and beyond the condenser, partly as a fine white powder, and partly as a solid mass. A brown tarry substance remained unvolatilized. A portion of the sublimate was sealed up with water and boiled. The boiling was continued every day for a week, but the sublimate did not dissolve.

An attempt was made to titrate the sublimate as above, but it required one hour at 95° to dissolve it, and results of 108.6 per cent. and 106.2 per cent. were obtained, showing that the permanganate was reduced by the heat.

The Grützner method was next tried : " Into a glass stoppered flask put 5 cc. of solution containing about 0.15 gram of formaldehyde, about 1 gram potassium chlorate, 50 cc. decinormal silver nitrate, and 1 cc. nitric acid. The closed flask is gradually warmed in the water-bath with frequent shaking. The reaction is complete in one-half hour. The end of the reaction is easily seen when the solution becomes clear above the silver chloride. The excess of silver nitrate may be titrated or the silver chloride may be weighed."

A sample of trioxymethylene was obtained from E. Merck, and portions were dried in the steam oven. Various experiments were made as to the best form of bottle, time, temperature, light, etc. By heating in blackened water to 80° C. and then one-half hour between 80° and 90°, filtering rapidly, and drying at 200° to constant weight, a pure white silver chloride was obtained, but the results in twenty determinations varied from 91 per cent. to 120 per cent. No reason could be found for this variation except in the inconstancy of the reaction. The Grützner method, then, seems to be altogether unreliable.

The Blank and Finkenbeiner method is as follows : " 1 gram trioxymethylene or 2 cc. formaldehyde is placed in a flask and 25 cc. of double normal soda solution added. Then 50 cc. of hydrogen dioxide, of strength 2.5 per cent. or 3 per cent. is added cautiously, the addition lasting three minutes. Allow stand two to three minutes and titrate with sulphuric acid, using litmus."

The commercial hydrogen dioxide contained acid, which was either neutralized or titrated, usually the former. The trioxy-

methylene was found to dissolve easily in the solution on the addition of the hydrogen dioxide. It was found that it is necessary to allow the flask to stand ten minutes before titrating. Results were as follows:

	Per cent.
Allowed to stand ten minutes cold.....	92.2
Heated slowly ten minutes.....	91.9
Sample dried by heating in flask to 85° for fifteen minutes with slow stream of natural gas.....	95.8
Sample heated to 85° for one hour, then a slow stream of natural gas passed for ten minutes.....	96.9
Gas passed for seven hours cold.....	96.4
Heated one hour at 85°, gas passed fifteen minutes, and then allowed to stand over calcium chloride five days.....	97.5

These results showed that the trioxymethylene contained water, and that, in the limited time allowed, it was practically impossible to dry it. The substance is almost as volatile as water, especially when warmed, and long standing in desiccators seemed the only way of drying it thoroughly. It was impossible to tell when the substance was dry, as when it apparently contained as much as 8 per cent. of water it was powdery, not sticking to glass, nor showing the slightest dampness. This explains the variable results of the earlier experiments and will prove of value in interpreting the results.

The Legler method is as follows: "To a sample of formaldehyde in a flask a sufficient excess of normal ammonia is added, allowed to stand tightly corked, and titrated back, using litmus, to which hexamethylene tetramine is neutral."

According to G. Lösekann,¹ the amine is monobasic to methyl orange, and must be titrated to a full red. It was decided to use methyl orange in order to avoid error from the presence of carbon dioxide.

W. Eschweiler² states that accurate results can be obtained only by allowing to stand five days or by boiling for one hour. Carl E. Smith³ states that it is necessary to allow to stand only fifteen minutes.

G. L. Taylor⁴ directs to allow to stand twelve hours, and L. F. Kebler⁵ says: "It is undesirable to report results on a reaction

¹ *Ber. d. chem. Ges.*, 22, 1565.

² *Ibid.*, 22, 1929.

³ *Am. J. Pharm.*, Feb., 1898.

⁴ *Ibid.*, April, 1898.

⁵ *Ibid.*, Sept., 1898.

of less than six hours' duration. * * * Neither were the results constant for duplicate of the same sample. * * * In my opinion, the only reason that Professor Smith arrived at the results he did was because the number of samples worked on was too limited."

It was decided to boil one hour. Trials on the same sample showed that practically the same result was obtained by allowing to stand eighteen hours at 16° , and one hour at 100° ,—93.1 per cent. for the former and 93.5 per cent. for the latter. The work was done with prescription bottles holding from 2 to 4 ounces, with soft rubber stoppers. Several attempts were made to dry the trioxymethylene, but as no 100 per cent. results could be obtained it was concluded that it was impossible to dry it in the limited time allowed for the first series of experiments.

A sample of commercial formaldehyde was tested, boiling in 2-ounce bottles for one hour, and titrating to full redness with methyl orange. The results were 37.34 per cent., 37.44 per cent. and 37.35 per cent. The Blank and Finkenbeiner method gives for this sample 37.30 per cent. These two methods are therefore in practical accord.

The chief difficulty in using the Legler method is the volatility of the normal ammonia. Carl E. Smith¹ proposes a way of getting rid of the standard ammonia by liberating ammonia from ammonium chloride by means of normal soda. In these experiments, the principal difficulty from the ammonia has been, not the loss of strength in the standard solution but the loss during the determination. This is not remedied by Professor Smith's modification.

By the following scheme both these sources of error are removed: Prepare a normal solution of sulphuric acid. Make up an approximately normal solution of ammonia, the exact strength being immaterial. Procure several 3-ounce prescription bottles with smooth sides and close-fitting soft rubber stoppers. Prepare a methyl orange solution. Procure a boiler in which the bottles may be immersed to the neck without upsetting (a large beaker will do). Take as much of the sample as will contain 0.5 gram of formaldehyde. Measure with the pipette, 25 cc. of the ammonia solution into each of the bottles, and to half of them add a sample of formaldehyde; stopper tightly. If the necks of the bottles are

¹ Am. J. Pharm., Feb., 1898.

small, the stoppers need not be tied down. Place the bottles in the boiler, add cold water to the necks, and heat to boiling. Boil for one hour, and cool by running in cold water slowly, being careful not to allow the cold water to touch the hot bottles. Titrate with sulphuric acid and methyl orange, *to the first indication of a color change*. Take the difference between the readings for the blanks and those for the samples, as the ammonia consumed, in normal cubic centimeters. Of this difference, 1 cc. equals 0.0601 gram of formaldehyde.

Trials were made on the sample of trioxymethylene which was previously used, but which had been standing for one year. Results were obtained as follows: 99.8, 98.5, 100.0, and 100.1 per cent. On a sample of commercial formaldehyde, these results were obtained: 38.0, 37.7, 37.6, 37.8, 37.8, 38.1 per cent. As this work was done at night, probably better results could be obtained under better conditions.

These experiments indicate that Lösekann obtained good results by titrating to a full red, because the loss during the titration about equals the amount of acid added between the first color change and the full red; that is, about 0.25 cc. By following Lösekann's directions, fairly good results may be obtained with normal ammonia solution, without the use of a blank. The rubber stopper changes its shape during the heating, and probably a glass-stopper would be better if convenient, and if a secure fit could be made. From the results of these experiments it is observed that the reaction of the Legler method is quantitative, and that the results are as accurate as the means will allow. The same may be said of the Blank and Finkenbeiner method.

The Legler method has the advantage that it is cheaper, more convenient, and less subject to error from impurities than the sample. In using the Legler method, the maximum results can be obtained by boiling for one hour.

It must be remembered that the errors in the Legler method do not balance each other. The tendency is toward low results. Therefore, in any series of results, the higher results are likely to be the better. A blank determination is necessary. In the titration a correct end-point is very important. In both the Legler and the Blank and Finkenbeiner methods, any acid present must be accounted for.

THE INDIRECT WEIGHING OF QUANTITATIVE PRECIPITATES. A RAPID AND ACCURATE METHOD FOR DETERMINING THE WEIGHT OF A PRECIPITATE WITHOUT SEPARATING IT FROM THE LIQUID FROM WHICH IT WAS PRECIPITATED.

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THANKS to the precision of the modern analytical balance, a gravimetric analysis, which consists essentially in the conversion of a weighed quantity of the substance to be assayed into an insoluble form, freeing it from impurities by washing, and drying and weighing it in the new form, is a process which is exact almost to the limit of perfection. But the difficulties in the way of properly preparing the material in a pure condition for subsequent weighing are many. The tendency of many precipitates to dissolve in the liquid used for washing out impurities, the mechanical adhesion of these impurities to the precipitated substance, and finally the difficulty of separation of the precipitate from the filtering medium, are too familiar to every analyst to need emphasis here. Many devices have been resorted to in order to obviate the errors arising from these causes, with the general result that an accurate gravimetric analysis is a process which requires considerable time for its completion and great care in its manipulation.

The disadvantages just alluded to have resulted in a very general attempt to devise volumetric methods which can be carried out with more ease and rapidity. Generally speaking, however, these volumetric methods, which are based upon the measurement of volumes of liquids which are known to contain definite proportions of the materials to be used, are open to serious criticism because of their inherent sources of error. Inaccuracies in calibration of the measuring apparatus, fluctuations in volume of solution due to changes in temperature, and changes in the composition of the dissolved material, give rise to serious errors, which are difficult to prevent and which greatly impair the value of this method of analysis.

It is obvious, therefore, that neither of these two classes of methods can be said to possess both of the requirements of an

ideal method of analysis, *viz.*, accuracy and rapidity. The desirability of some simple method by means of which the weight of a precipitated substance could be accurately determined without the necessity of first completely separating it from the liquid from which it was precipitated is apparent. Such a method would have the accuracy of a gravimetric process, without its attendant objectionable features, and would be more accurate than many of the volumetric methods. So far as I have been able to learn, no such method has been suggested up to the present time. That the operation is possible, however, is shown by the discussion below. That it is not only possible, but practicable and capable of wide application, is shown by the analytical data presented in a subsequent portion of this paper.

THE THEORETICAL DISCUSSION OF THE PROPOSED METHOD.

The formulas which are given below are based on facts which are so well known as to seem axiomatic; namely, that the weight of any substance is equal to its specific gravity times its volume ; and conversely, that the volume of any substance is equal to its weight divided by its specific gravity.

If now a certain definite volume (which may be represented by b) of a mixture of a liquid and a solid, or precipitate, be weighed, the weight thus obtained is obviously equal to the sum of the weights of the liquid and the precipitate. Or, if the weight found be represented by a and that of the precipitate and liquid by x and y respectively, then

$$a = x + y. \quad (1)$$

Now the weight of the liquid v is, as was stated above, equal to its volume times its specific gravity. Its volume is obviously the total volume of the mixture minus that of the precipitate, and the volume of the precipitate is its weight divided by its specific gravity. Or, if we represent the volume of the precipitate by v , and that of the liquid by v' , and their specific gravities by d and d' respectively, then

$$y = v'd', \quad (2)$$

$$v' = b - v, \quad (3)$$

$$v = \frac{x}{d}. \quad (4)$$

Combining 2, 3, and 4, we have

$$y = (b - \frac{x}{d}) d'. \quad (5)$$

Substituting this value for y in (1) the formula becomes

$$a = x + \left(b - \frac{x}{d}\right)d', \quad (6)$$

or $x = \frac{d(a - bd')}{d - d'}. \quad (7)$

In this formula a , the total weight, and b , the total volume, are known; d , the specific gravity of the precipitate, is constant for precipitates of the same substance and can be determined once for all; and d' , the specific gravity of the liquid, can easily be determined. From these factors the value of x , the unknown weight of the precipitate, can be calculated.

From the above discussion it appears that in order to determine the weight of any precipitate without separating it from the liquid from which it was precipitated, it is only necessary to transfer the mixture to a vessel, the exact volume and weight of which is known; weigh the whole; then draw off a portion of the liquid and determine its specific gravity. From this data and the known specific gravity of the precipitate, the weight of the latter can easily be calculated by means of the formula given above. This formula is a general one, and the process is, therefore, applicable to all precipitates of which the specific gravity is known or can be determined. The one condition by which its application is limited is, that the specific gravity of the precipitate must be constant, or, in other words, that the precipitate must always have the same composition. Most quantitative precipitates are of definite and invariable composition and hence meet this requirement. A few, however, vary in character with varying conditions of precipitation. This method of procedure could be used for determining the weights of such precipitates only when the conditions under which they were formed were so controlled as to insure uniformity in the composition of the precipitate.

Furthermore, the same formula, or modifications of it, will serve for other purposes. For example, if a known quantity of some substance is so treated as to produce a known weight of precipitate the specific gravity of the latter may be determined by a process identical with that described above. In this case x , the weight of the precipitate, will be known and d , its specific gravity, unknown. In order to simplify the calculation, the formula may be rearranged as follows:

$$d = \frac{d'x}{bd' + x - a}. \quad (8)$$

Since no very satisfactory method for determining the specific gravity of solids in finely divided or amorphous condition has heretofore been proposed, the importance of this application of the formula is apparent. It is especially valuable in determining the specific gravity of those precipitates which decompose or change in composition during the washing and drying which is necessary in order to obtain them in a pure form.

Again, in case a substance can be readily obtained in pure condition, its specific gravity may be easily determined by placing a weighed quantity of it in the weighing-bottle and filling the latter with pure water, and weighing the whole. Since the specific gravity of the liquid in this case is known, no further data need be determined. The specific gravity of the solid can be computed from the formula (8), d' being a constant (*i. e.*, the specific gravity of water at the temperature at which the weighing is made), and bd' likewise a constant for the same weighing-bottle.

Further, since this method of determining specific gravity can be carried out very rapidly, it may serve as a means of determining the rate of change in composition of certain variable precipitates, as, for example, the rate of dehydration of the hydrated oxides of aluminum or iron. Some data bearing on this application of the formula was accidentally accumulated during the investigations upon the accuracy of this method of obtaining weights of precipitates, and will be published at some later time.

METHODS OF OPERATION.

Briefly stated, the principle upon which this new method for determining the weight of quantitative precipitates is based, is that if the weight of a definite volume of a mixture of two substances, whose specific gravities are known, be determined, the proportion of each which is present in the mixture may be calculated. An indirect determination of the weight of a precipitate without previously separating it from the liquid from which it was precipitated, based upon this principle, consists of the following processes : first, a determination of the weight of a measured volume of the precipitate and mother-liquor ; second, the separation of a correct sample of the liquid from the precipitate ; third, a determination of the specific gravity of this liquid; and fourth, a calculation of the weight of the precipitate by means of the

formula described above. A previous knowledge, or determination, of the specific gravity of the precipitate is, of course, necessary. The details of these operations and precautions to be observed in each are described below.

Specific Gravity of the Precipitate.—It should be noted that the same accuracy in the determination of the specific gravity of the precipitate as in that of the liquid is not necessary. In practical work with such mixtures, the relative amount of precipitate present will always be small and any inaccuracy in the determination of its specific gravity will produce a correspondingly small error.

None of the methods which have been proposed for the determination of the specific gravity of a solid substance are very well adapted to work with finely divided or amorphous precipitates. Determinations based upon the loss of weight of the material when immersed in a liquid require the preparation of the substance in a perfectly pure and dry condition, which in itself is as difficult as the preparation of such precipitates for quantitative analysis, and the use of specially constructed apparatus. Methods based upon a measurement of the volume, or displacing power, of a weighed quantity of the substance are exceedingly unsatisfactory when applied to substances in powdered form, because of their tendency when dry to enclose air. It was found that methods based upon the use of the new formula as arranged for specific gravity (8) afforded by far the most satisfactory method for this purpose. As has been pointed out, this formula may be applied in two ways: first, by using a known amount of the material with pure water as the liquid for completing the desired volume, and second, by producing a known amount of the desired material by precipitation, weighing the mixture, and afterward determining the specific gravity of the liquid.

In all the following work a Geissler specific gravity bottle, or pycnometer, with a thermometer ground in as a stopper and a capillary overflow tube provided with a glass stopper, was used as the vessel in which a definite volume of liquid, or mixture of solid and liquid, was weighed. Such a pycnometer having been selected and its weight and volume once accurately determined, it can be used for a long series of determinations without the necessity of recalibration, since changes in its weight or volume are very slight, or practically none at all. Two of these pycnometers

were used, one having a capacity of approximately 100 cc. and the other of about 50 cc. These were calibrated as follows: The pycnometer was carefully cleansed and dried and its weight accurately determined. It was then filled with distilled water, which had been recently boiled and then cooled to a temperature slightly below that at which the bottle was to be calibrated. The thermometer was inserted and the temperature of the water allowed to rise slowly, the pycnometer being frequently shaken to insure uniform temperature throughout the whole. When the thermometer indicated 20° (that being adopted as the temperature most convenient for the working conditions of this laboratory), the overflow tube was closed, the outside of the pycnometer carefully dried, and the whole immediately weighed. The pycnometer was emptied, refilled, and reweighed several times until an exact knowledge of its water content at 20° was obtained. This weight was then divided by 0.998213 (the specific gravity of water at this temperature), and the result taken as the volume of the pycnometer. The weighings were all corrected for a slight difference in the length of the balance arms but were not reduced to the weight *in vacuo*, as this was not deemed necessary for the purpose of ordinary analytical work. In order to determine the specific gravity of any insoluble substance of which a quantity of pure material was available, it was only necessary, then, to introduce a weighed quantity of it into a pycnometer which had been calibrated as described above; fill the latter with pure distilled water, properly cooled; bring the mixture to the temperature adopted in calibration; and complete the weighing as before. The specific gravity of the precipitate was then calculated from the formula. If the substance in question was in the form of a dry powder a little water was added to it after it had been weighed and the mixture stirred thoroughly to insure complete wetting of the material and exclusion of enclosed air bubbles. In case no supply of pure material of the substance whose specific gravity was to be determined was available, or could be prepared only with difficulty, the process was carried out exactly as will be described below for the indirect weighing of precipitates. In this case it was necessary to start with a known amount of some soluble material which was subsequently quantitatively precipitated in the desired form. The details of the method will appear in a subsequent paragraph.

Loevinsohn¹ has shown that the state of subdivision or mass of a substance has no effect upon its specific gravity, hence it is only necessary to insure that the composition of the precipitate shall be invariable in order that its specific gravity shall be constant, no matter what the conditions under which it was precipitated may be. The specific gravity of any invariable quantitative precipitate having been once accurately determined, this factor may be used for all subsequent indirect determinations of the weight of precipitates of this substance.

Weight of a Definite Volume of the Mixture.—Any apparatus, the exact volume of which is known, might serve as a weighing-bottle for the mixture, but since the volume and, conversely, the specific gravity of a liquid are affected by changes of temperature, a means of controlling or determining the latter is essential. A very small neck or opening which may be closed, in order to prevent evaporation of the liquid during weighing, is also very desirable for accurate work. The Geissler specific gravity bottle already mentioned is admirably suited to these needs.

The weighing-bottle having been prepared, the substance to be weighed was precipitated according to the method used in the ordinary analysis. After precipitation was complete, the mixture was cooled to a temperature slightly below that at which the pycnometer was calibrated. (The total volume of the mixture should not exceed two-thirds that of the pycnometer. If greater than this, the excess of liquid was removed by drawing it off through a filtering pipette.) A funnel with a short stem was placed in the neck of the pycnometer and the precipitate and mother-liquor were washed into it by means of a fine jet of cold water. After the precipitate was all washed in, the volume was completed with water which had been properly cooled, the water being allowed to flow down the sides of the pycnometer so as not to disturb the precipitate below and cause it to rise in the neck of the bottle. A very small amount of certain precipitates will rise to the surface by "creeping." In case this occurred, the material on the surface of the liquid was gently tapped with the bulb of the thermometer several times before inserting the latter. This generally sufficed to cause the floating particles to settle and thus prevent any loss of the precipitate. After the thermometer had been inserted, the capillary opening was closed with the

¹ Inaug. Diss., Berlin, 1883; abs. in *Ber. d. chem. Ges.*, 12, 22.

finger, the bottle inverted, and its contents thoroughly mixed by shaking, so as to insure uniformity in the dilution of the liquid. This was repeated several times while the temperature of the liquid was rising to the desired point. When the thermometer indicated 20° the pycnometer was closed, dried, and immediately weighed. Except in very rare cases, no appreciable change in temperature occurred during the weighing, since the temperature of the balance case was usually but very slightly above that of the pycnometer. The weight thus obtained minus that of the pycnometer gave that of the volume of the mixture which the latter contained.

Separation of the Liquid from the Precipitate.—In order that the sample of liquid, which was withdrawn to be used in the determination of its specific gravity, should exactly represent the composition of the whole of the liquid, it was necessary that the process be rapid enough to prevent any concentration by evaporation, that the liquid should not be diluted by coming in contact with damp or wet apparatus, and that its separation from the precipitate should be complete. The ordinary method of filtration would generally result in a change in specific gravity through evaporation, and would be a return to one of the objectionable features of the usual methods of analysis. Two methods for accomplishing the desired result suggested themselves: first, the withdrawal of the desired sample by means of a filtering pipette, and second, a mechanical subsidence of the precipitate by means of a centrifugal and subsequent drawing off of a sample of the clear supernatant liquid. The use of a filtering pipette would afford a very convenient and rapid means of withdrawing a portion of clear liquid from the mixture, if the precipitate were in granular or crystalline form, but in the case of those precipitates which tend to clog up the filter or are so finely divided as to partially pass through the ordinary filtering media, the process is much less satisfactory. Moreover most of the forms of filtering pipette which have yet been suggested are more or less difficult to clean and dry rapidly.

Hence, in nearly every determination which was made in the present work the second method of separating the liquid from the precipitate was employed. The only centrifugal which was available was an old form of the Babcock milk tester. This was used with very satisfactory results. The separation was accomplished

as follows: The mixture in the pycnometer was shaken gently to insure uniform composition of the liquid and a portion of it poured into a large, clean, dry test-tube. The latter was placed in the centrifugal and whirled until the precipitate settled completely, leaving a clear, supernatant liquid. For most of the precipitates this required less than one minute. Barium sulphate and aluminum hydroxide required a little longer, but in no case was it necessary to spin the apparatus longer than three minutes. Evaporation of the liquid during this time was, of course, very slight and could be entirely prevented by closing the test-tube with a cork. As soon as the supernatant liquid was free from floating particles of the precipitate, a sufficient amount of it to fill the smaller pycnometer was drawn up into a dry pipette and its specific gravity determined. Duplicate samples drawn from various depths in the tube showed no appreciable variation in density.

Specific Gravity of the Liquid.—The determination of the specific gravity of the liquid component of the mixture is the most critical operation in the whole process. A single computation of the weight of a precipitate by means of the new formula will suffice to show that any very large error in the fifth decimal place of the factor for the specific gravity of the liquid will produce a small error in the fourth decimal place (or tenths of milligrams) of the weight obtained. It is therefore essential that the method to be adopted for determining the specific gravity of the liquid shall be capable of giving results with considerable accuracy to the fifth decimal place. This excludes the use of ordinary areometers, specific gravity balances, etc., and limits the operator to the use of specific gravity bottles of the best form. It has been shown by many analysts, however, that the Geissler pycnometer if carefully controlled will give results which are very accurate to the fifth decimal place. Extreme care, such as is used in the best of physical-chemical operations, will give results very closely approximating the truth in the sixth place, but such accuracy as this is not necessary for ordinary analytical work.

This method of determining the specific gravity of a liquid was therefore chosen as the one best adapted to the purposes of the present work. The process of such a determination is too familiar to all analysts to need detailed description. The pycnometer was filled with the liquid in question in exactly the same manner as it

was filled with water in calibration, and weighed under the same conditions. The weight of the liquid thus obtained, divided by the weight of the same volume of water, corrected for the specific gravity of water at the temperature of the weighing, gave the specific gravity of the liquid.

Calculation.—The calculation of the weight of the precipitate from the data obtained as described above was a comparatively simple process. The factor b in the formula, representing the volume of the large pycnometer, is a constant which in every calculation is to be multiplied by the specific gravity of the liquid. A table showing the product obtained by multiplying this factor by each of the digits, was prepared, which greatly facilitated the calculation.

Effect of Variations in Formula for Precipitate.—The exact composition of some of the common quantitative precipitates when in the moist condition is not known, since they may contain some chemically combined water which they lose on being dried for an analysis. Such a knowledge is not absolutely necessary for the purpose of this method of determining their weight, however. If a certain formula be assumed to represent the composition of such a precipitate and its specific gravity calculated on this basis, it is obvious that a weight calculated from the specific gravity thus obtained will be correct even though the formula which was adopted does not correctly represent the nature of the substance. The error in the determination of the specific gravity will be repeated in the opposite direction in the subsequent calculation and a correct result will thus be obtained.

It is, however, absolutely essential that the nature of the precipitate shall be the same under the conditions of the determination of its weight as under those which accompany the determination of its specific gravity. For those precipitates whose composition is likely to vary with the conditions under which they are produced, the determination of their specific gravity by the same process as is to be used later in weighing is the best method to pursue, since it will obviate any errors due to change in the nature of the precipitate. As has been shown, it is possible to do this by producing the precipitate in such a manner that its weight may be known, and its specific gravity calculated by the proper arrangement of the new formula.

EXPERIMENTAL WORK.

In order to test the accuracy of the new method of obtaining the weights of quantitative precipitates and also to compare this method with the older ones with regard to simplicity of manipulation, a large number of determinations of the weights of precipitates obtained from chemically pure material by the best methods of quantitative precipitation were made. In general those precipitates which are of considerable technical importance and which are subject to peculiar disadvantages when weighed by the usual gravimetric methods, were selected for this experimental work.

Estimation of Chlorine as Silver Chloride.—Rodwell¹ states that the specific gravity of silver chloride is 5.505 at 0° C. and 4.919 at the melting-point. Mohr² gives the figure 5.7 as the specific gravity of silver chloride but does not state the conditions under which the determination was made. Loevinsohn³ gives the following as the average results of several determinations of the specific gravity of silver chloride in different physical forms: freshly precipitated, 5.5667; dried, 5.5667; melted, 5.5549. Schröder,⁴ in his work on the molecular volume of silver chloride, obtained results for its specific gravity which varied from 5.517 to 5.594 with an average of 5.553.

These results vary so widely as to make it impossible to determine from them what the true value for the specific gravity of silver chloride is. It was therefore necessary to make a series of determinations, in order to obtain a correct factor to be used in the subsequent work of determining chlorine as silver chloride.

Since silver chloride decomposes quite rapidly when exposed to the light, several known quantities of pure silver chloride were produced immediately before beginning this work as follows: Measured portions of a standard hydrochloric acid solution (the exact chlorine content of which had been previously determined) were precipitated with silver nitrate according to the method usually adopted for that purpose. The precipitate in each case was transferred to a large test-tube and whirled in the centrifugal. In this way the precipitate was quickly collected in a compact mass at the bottom of the tube and the supernatant liquid could

¹ Proc. Roy. Soc., 25, 280.

² Pogg. Ann., 113, 655.

³ Inaug. Diss., Berlin, 1883.

⁴ Ann. Chem. (Liebig), 192, 295.

be almost entirely drawn off by means of a filtering pipette without disturbing the precipitate. The latter was washed with hot distilled water in this way until the washings gave no test for silver. The pure silver chloride thus obtained was perfectly white, the process being of so short duration as to prevent any decomposition.

The precipitate was immediately washed into a pycnometer, the latter filled with pure distilled water and weighed under the conditions outlined in the previous description of the method for determining specific gravity of precipitates. The following are the results of the determinations.

TABLE I.—SPECIFIC GRAVITY OF SILVER CHLORIDE.

	Hydrochloric acid taken. cc.	Silver chloride equivalent. Gram.	Calculated spe- cific gravity.
1	30	0.4573	5.5591
2	40	0.6098	5.5561
3	35	0.5335	5.5455
4	45	0.6860	5.5680

Average, 5.5570

A sample of chemically pure sodium chloride was finely pulverized, dried in an air oven at 120° for an hour, and several samples of this powder weighed out for analysis. Each weighed sample was dissolved in distilled water, the solution heated to boiling, and the chlorine precipitated by silver nitrate solution, according to the usual method. The mixture was then cooled down to about 18°. It was then washed into the large pycnometer, brought to the proper temperature, and weighed. The precipitate settled so completely during the weighing that it was not necessary to whirl the mixture in the centrifugal in order to obtain a clear liquid for the specific gravity determination. After weighing, therefore, the mixture was cooled slightly, a portion of the clear supernatant liquid drawn off, transferred to the smaller pycnometer, weighed as soon as it reached the proper temperature, and the specific gravity calculated. From these data the weight of the silver chloride found was calculated. The following are the results which were obtained:

TABLE II.—DETERMINATIONS OF CHLORINE IN SODIUM CHLORIDE.

	Sodium chloride taken. Grams.	Silver chloride found. Grams.	Chlorine equivalent. Gram.	Chlorine found. Per cent.
1	0.8164	1.9998	0.4946	60.58
2	1.0205	2.5085	0.6202	60.76
3	1.0342	2.5320	0.6262	60.56
4	0.6186	1.5233	0.3757	60.73
5	0.4823	1.1851	0.2931	60.76
6	0.6877	1.6899	0.4179	60.75

The theoretical amount of chlorine in sodium chloride is 60.60 per cent. The results shown above are therefore within the limit of experimental error. They are no better than may be obtained by the ordinary methods of weighing, however. These determinations were the first that were made by the new process and it is probable that with more experience in manipulation better results would have been obtained. The process, however, does not offer any especial advantage over the usual gravimetric analysis in the case of a precipitate which is so easily prepared for weighing as is silver chloride. Should some substance which would render the washing of the precipitate tedious or difficult to complete be present in the solution, this new method might be of value.

Estimation of Sulphur as Barium Sulphate.—Several determinations of the specific gravity of barium sulphate by the older methods have been published. Mohr¹ gives 4.446 as the result obtained when the dried precipitate was used. Karsten² used ignited material and obtained 4.2003 as its specific gravity. Rose³ made two determinations, using freshly precipitated salt with an average result of 4.5262. Schröder,⁴ during his work on molecular volumes, made several determinations under different conditions and gives results varying from 4.022 to 4.512 with a mean value of 4.330. Wiedemann⁵ made four determinations, using water at 14.9° as the standard of comparison. He obtained very concordant results, the average being 4.3962. None of these results being satisfactory for the present work, preliminary determinations of the specific gravity of barium sulphate were necessary. A quantity of pure barium sulphate was dried in the

¹ See Böttger's "Tabell. über dem Spez. Gew. Körpern."

² Schweigger's *Journal*, 65, 394.

³ Pogg. *Ann.*, 75, 409.

⁴ *Ibid.*, 106, 226.

⁵ *Ibid.*, [5], 15, 371.

oven at 140° and varying amounts of this material were weighed out for the determination of specific gravity. Each weighed portion was washed into the pycnometer and the latter filled with distilled water and the determination of specific gravity completed as usual. The following results were obtained :

TABLE III.—SPECIFIC GRAVITY OF BARIUM SULPHATE.

	Barium sulphate taken. Grams.	Calculated spe- cific gravity.
1	3.7251	4.2982
2	1.6317	4.3330
3	2.0868	4.3225
4	1.2738	4.3293
5	3.0931	4.3000
6	2.8593	4.2791
7	1.7795	4.3062
Average,		4.3098

The factor 4.31 was assumed as representing the correct value for the specific gravity of barium sulphate and was used in all subsequent determinations of the weight of precipitates of the latter.

A quantity of chemically pure potassium sulphate was finely pulverized, dried in the air-oven, and cooled in a weighing-bottle. Six samples were weighed out from this bottle into separate beakers. Each sample was dissolved in distilled water, 10 cc. of concentrated hydrochloric acid added, the solution heated nearly to boiling, a slight excess of barium chloride solution added, and the mixture boiled for a few minutes. After standing for a short time a part of the clear supernatant liquid was drawn off so as to reduce the total volume to about half that of the large pycnometer. The remainder of the mixture was then cooled, washed into the pycnometer, and the latter filled and weighed as usual. After this weighing the liquid in the pycnometer was thoroughly mixed by shaking, then poured into a large test-tube, the latter placed into the centrifugal and whirled until the precipitate had completely subsided. This required two or three minutes and the temperature of the liquid was raised several degrees. As soon as the supernatant liquid became clear, a portion of it was drawn off, cooled, transferred to the smaller pycnometer and its specific gravity determined. From the data thus obtained the weight of the barium sulphate precipitate was calculated. The following are the results obtained :

TABLE IV.—DETERMINATIONS OF SULPHUR IN POTASSIUM SULPHATE.

	Potassium sulphate taken. Grams.	Barium sulphate found. Grams.	Sulphur equivalent. Gram.	Sulphur found. Per cent.
I	2.4887	3.3581	0.4612	18.53
2	2.8379	3.8583	0.5299	18.67
3	2.2032	2.9823	0.4096	18.58
4	0.9574	1.2759	0.1753	18.32
5	0.6000	0.8063	0.1107	18.45
6	0.6459	0.8664	0.1190	18.42

The theoretical amount of sulphur in potassium sulphate is 18.40 per cent.

The determinations recorded above are all that were made by the new method and may therefore be regarded as showing what may be expected of this method in ordinary work. They show that if the amount of barium sulphate precipitated is not too large, very satisfactory results are obtained. Even with the very large amounts of precipitate obtained in Nos. 1, 2, and 3 above, the results compare very favorably with those which it is possible to obtain by the ordinary methods of weighing this precipitate. The whole process of determining the weight of barium sulphate precipitate by this method requires less than thirty minutes' time. The very difficult and tedious process of washing the barium sulphate free from impurities is unnecessary and all danger of loss of precipitate, because of its slight solubility in the water used for washing it, is avoided. This method as applied to the determination of the weight of a precipitate of barium sulphate may therefore be carried out with very much more rapidity and is much less susceptible to error than any of the methods now in use.

Estimation of Calcium as Calcium Oxalate.—The only results of determinations of the specific gravity of calcium oxalate are those published by Schröder.¹ He gives the following values for the precipitate at 4°: 2.181, 2.182, and 2.200. Previous work along this line being so meager, it was necessary to make a sufficient number of determinations to insure a very reliable average result. No pure calcium oxalate being available, a few perfect crystals of Iceland spar were selected as the starting-point for this work. These were ground to a fine powder in an agate mortar. The powder was then dried thoroughly and three portions of it weighed out into separate beakers. These were each dissolved in dilute

¹ Ber. d. chem. Ges., 12, 561.

hydrochloric acid, the solution heated to boiling, ammonia and a slight excess of ammonium oxalate added, and the whole boiled gently for a few minutes. Souchay and Lenssen¹ have shown that under these conditions a stable precipitate having the composition $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ is formed. These precipitates were washed by decantation, as described in the case of silver chloride, until free from chlorides, and their specific gravity determined by weighing with pure water. The results obtained are indicated by Nos. 1, 2, and 3 in the table below. From the same material a fourth portion of exactly 10 grams was weighed out, transferred to a liter flask, and dissolved in dilute hydrochloric acid. The volume was completed to the mark and four aliquot portions immediately drawn off before any appreciable change in volume due to rise in temperature had occurred. The calcium in these solutions was then precipitated as described above. The specific gravity of these precipitates was then determined by the usual method without separation from the mother-liquor. The results obtained are indicated by Nos. 4 to 7 inclusive in the table below.

TABLE V.—SPECIFIC GRAVITY OF CALCIUM OXALATE.

	Calcium carbonate taken. Grams.	Calcium oxalate equivalent. Grams.	Calculated spe- cific gravity.
1	1.2594	1.8261	2.2524
2	1.5230	2.2083	2.2461
3	1.4184	2.0567	2.2418
4	1.0000	1.4500	2.2425
5	0.5000	0.7250	2.2528
6	1.0000	1.4500	2.2433
7	0.5000	0.7250	2.2470

Average, 2.2465

Three aliquot portions of the solution of Iceland spar in hydrochloric acid described above were measured out, and two other samples of the finely ground material were weighed out and dissolved in dilute hydrochloric acid. The calcium was precipitated from the boiling solution by ammonia and ammonium oxalate and the precipitates allowed to stand until cool. The indirect weighing of these precipitates was then carried out as previously described, with the following results:

¹ *Ann. Chem. Pharm.*, 100, 322.

TABLE VI.--DETERMINATIONS OF CALCIUM IN ICELAND SPAR.

	Calcium carbonate taken. Grams.	Calcium oxalate found. Grams.	Calcium equivalent. Gram.	Calcium found. Per cent.
1	1.0000	1.4483	0.4000	40.00
2	0.5000	0.7266	0.2007	40.14
3	0.5000	0.7251	0.2002	40.04
4	1.0009	1.4542	0.4019	40.15
5	1.0785	1.5595	0.4207	39.97

The theoretical amount of calcium in calcium carbonate is 40.04 per cent. The results obtained are therefore well within the limits of experimental error. The weighing of the precipitate by this method does not require more than thirty minutes' time, so that a complete gravimetric determination of calcium by this method may be made in less than one hour and the results are as accurate as can be obtained by the best of the present methods. The washing of the precipitate and its subsequent conversion into carbonate or oxide by ignition are therefore unnecessary.

Estimation of Phosphoric Acid as Ammonium Phosphomolybdate.—The estimation of phosphoric acid is one of the most important as well as one of the most difficult problems which the technical analyst has to solve. Its precipitation as ammonium phosphomolybdate is now almost universally adopted, because this compound serves to effect the separation of phosphoric acid from other bodies and possesses the added advantage of being a readily subsiding precipitate. Earlier experimenters have considered that the composition of the compound is somewhat variable and that its conversion into some more stable form prior to the final weighing is therefore necessary. More recently Hundeshagen,² in his analytical studies of this compound, has shown that its composition under all conditions, when free from molybdic acid and other impurities, is $12\text{MoO}_3 \cdot \text{PO}_4 \cdot 3\text{NH}_4$. It is quite difficult to obtain the precipitate free from impurities, however, and nearly all the gravimetric methods now in use require the solution of the precipitate in ammonia and its subsequent precipitation as magnesium ammonium orthophosphate, the latter being ignited and weighed as magnesium pyrophosphate, or titrated volumetrically. There are numerous difficulties in this process. Bergami³ is of the opinion that magnesium oxide is frequently thrown out along

¹ Fresenius' "Quantitative Analysis," p. 199.

² *Chem. News*, 60, 168, 177, 188, 201, 215.

³ Bull. 43, Division of Chemistry, U. S. Dept. Agr., p. 99.

with the phosphate precipitate, which produces too high results. Furthermore Gooch and Austin¹ found that if too much ammonium salts are present in the solution the precipitate is apt to be partially converted into a metaphosphate on ignition, which will likewise yield too high results when calculated back to phosphoric acid. These difficulties have led to numerous attempts to execute the final determination directly upon the yellow precipitate. Carnot² has shown that, with proper precautions, the yellow salt may be reprecipitated from its ammoniacal solution, washed dried at 100°, and weighed. This method has not come into very general use, however, since great care must be exercised to prevent loss of the precipitate during washing. Pemberton³ has suggested a volumetric method for titrating the yellow precipitate, which has been modified by Kilgore⁴ so as to yield fairly satisfactory results. It is open to the general objections of all volumetric methods of analysis, however. Kilgore's results show that within certain limits a precipitate of constant composition, free from molybdic acid, may be obtained. The new method is, therefore, applicable to this precipitate. Its desirability is apparent, since it will avoid the danger of loss of the material, because of its slight solubility in the wash-water, and at the same time afford a simple gravimetric method for determining the weight of the precipitate.

No determinations of the specific gravity of this yellow precipitate have yet been published. It was therefore necessary to accurately determine this factor before attempting to test the applicability of the new method to the weighing of this precipitate. Two methods of procedure were adopted. For the first a quantity of the yellow precipitate, which had been accumulated in previous work, was carefully purified by repeated washing and portions of it suspended in pure water properly cooled and weighed in the pycnometer at 20° as usual. After weighing, the contents of the pycnometer were rinsed into a white dish, dissolved in a measured excess of carefully standardized potassium hydroxide solution and the excess of the latter titrated back with standard nitric acid according to Kilgore's method. From the amount of potassium hydroxide required, the weight of the ammonium phosphomolybdate

¹ *Am. J. Sci.*, 1899, pp. 187-198.

² *Bull. Soc. Chim.*, Paris, 1893, 343.

³ *This Journal*, 18, 382; 16, 278.

⁴ *Bull. 43, Division of Chemistry, U. S. Dept. Agr.*, p. 91.

present in the mixture was calculated. This weight and the weight of the mixture in the pycnometer afforded the data necessary for the calculation of the specific gravity of the precipitate. The results obtained are indicated by Nos. 1 to 4 inclusive in the table below. For the second series of determinations a quantity of pure disodium phosphate was obtained by recrystallization, and dried between filter-paper. A weighed portion of this was dissolved in water, and aliquot portions of this solution precipitated exactly as required by the Kilgore volumetric method, since this has been shown to give a precipitate free from molybdic acid. The specific gravity of these precipitates was determined by the usual method without separating them from the mother-liquor. Four determinations, using in each case 15 cc. of the solution which contained 0.01119 gram of disodium phosphate per cubic centimeter, were made, with the results indicated by Nos. 5 to 8 inclusive in the following table:

TABLE VII.—SPECIFIC GRAVITY OF AMMONIUM PHOSPHOMOLYBDATE.

	Ammonium phospho-molybdate equivalent. Grams.	Calculated specific gravity.
1	1.4600	4.011
2	1.4602	4.079
3	1.9405	4.050
4	2.9102	4.074
5	0.8793	4.040
6	0.8793	4.055
7	0.8793	4.086
8	0.8793	4.032

Average, 4.055

For the purpose of testing the accuracy of the new method of weighing to the phosphoric acid precipitates, seven determinations of the percentage of phosphoric acid in pure disodium phosphate were made. Two further aliquot portions were drawn from the solution which was used in the specific gravity determination; a second solution was made up and three aliquot portions of this were taken. Finally two small samples of the material were weighed in two beakers and dissolved in water. The phosphoric acid in each solution was precipitated as in Kilgore's method, the mixture cooled, and the indirect weighing of the precipitate completed as usual. The following are the results of the analyses, stated in the same order as mentioned above.

TABLE VIII.—DETERMINATIONS OF PHOSPHORIC ACID IN DISODIUM PHOSPHATE.

	Disodium phosphate taken. Gram.	Ammonium phosphomolybdate found. Grams.	Phosphorus pentoxide equivalent. Gram.	Phosphorus pentoxide found. Per cent.
1	0.1679	0.8796	0.03330	19.83
2	0.1679	0.8747	0.03309	19.71
3	0.3144	1.6554	0.06253	19.89
4	0.2695	1.4111	0.05339	19.81
5	0.3593	1.8962	0.07164	19.94
6	0.2328	1.2238	0.04630	19.84
7	0.2486	1.2974	0.04909	19.74

The theoretical percentage is 19.82

All calculations were based upon the formula $12\text{MoO}_3 \cdot \text{PO}_4 \cdot 3\text{NH}_3$, for the yellow precipitate. Carnot stated that the precipitate when dried at 100° contains water of crystallization as represented by the formula $24\text{MoO}_3 \cdot \text{P}_2\text{O}_7 \cdot 3(\text{NH}_4)_2\text{O} \cdot 3\text{H}_2\text{O}$. Whether or not this be correct, no error is produced by the assumption of the more commonly accepted formula since the latter was used in calculations of the specific gravity also. These determinations show that if proper care in manipulation is exercised, this simple method is capable of yielding very accurate results with this precipitate which has heretofore caused analysts so much trouble. The only extra precaution which is required in this application of the method is that the precipitate must always be thrown down under similar conditions, since otherwise it is apt to be contaminated by impurities.

Specific Gravity of Cuprous Oxide.—F. W. Clarke in his "Tables of Specific Gravity"¹ cites the following results of determinations of the specific gravity of this precipitate: 6.052 and 6.093;² 5.751;³ 5.750;⁴ 5.746;⁵ 5.300, 5.342, and 5.375.⁶

The limitations of our library have prevented my verification of these figures, or study of the conditions under which the determinations were made.

The cuprous oxide which is precipitated from boiling Fehling's solution by reducing sugars is supposed to be more or less hydrated. The degree of this hydration probably varies with the concentration of the solution, etc. Moreover, cuprous oxide is

¹ Bull. of the U. S. Geological Survey, 1886.

² Herapath: *Phil. Mag.*, 64, 321.

³ Karsten: *Schweigger's Journal*, 68, 394.

⁴ Leroyer and Dumas: Böttger's "Tab. Unters. d. Spez. Gew."

⁵ Playfair and Joule: *Mem. Chem. Soc.*, 3, 82.

⁶ Peroz: *J. prakt. Chem.*, 47, 84.

quite easily oxidized to the cupric condition. These facts make the preparation of a known quantity of pure cuprous oxide a somewhat difficult task. It is probable, however, that within the extremely narrow limits to the conditions of carrying out the reduction as prescribed by the methods now adopted by the Official Agricultural Chemists, the composition of the precipitate is practically invariable. The amount of precipitate produced varies with the time during which the sugar solution is boiled with the Fehling solution. Since it is almost impossible to keep this time always exactly the same, the use of a known amount of a reducing sugar in order to obtain a known amount of cuprous oxide is not sufficiently accurate for the purposes of this work. It was determined therefore to precipitate several quantities of the cuprous oxide according to the official method, wash them thoroughly, use the pure material thus obtained for the specific gravity determination, and afterwards dissolve the precipitate and determine the copper therein by some standard method. Five such precipitates were prepared and their specific gravity determined, the amount of copper present in each case being determined by titration with standard potassium cyanide solution. The following results were obtained :

TABLE IX.—SPECIFIC GRAVITY OF CUPROUS OXIDE.

	Potassium cyanide solution used. cc.	Cuprous oxide equivalent. Gram.	Calculated spe- cific gravity.
1	85.6	0.5040	5.7000
2	76.3	0.4532	5.7336
3	81.7	0.4853	5.6788
4	77.3	0.4591	5.7058
5	84.6	0.4476	5.6852
Average,			5.7007

The factor 5.7 was therefore assumed as representing very nearly the specific gravity of the cuprous oxide as precipitated under the conditions required by Allihn's method.¹ Since it is not necessary that the exact nature of the precipitate be known, or that the formula assumed to represent its composition be exactly correct, it was not deemed essential that any allowance for hydration of the precipitate be made. In all this work, therefore, the precipitate was considered as being simply cuprous oxide, and all calculations were made on this basis.

¹ Bull. 46, rev. ed., Division of Chemistry, U. S. Dept. of Agr., p. 35.

Determinations of Invert Sugar.—For the purpose of testing the accuracy of this method as applied to the weighing of cuprous oxide precipitated by invert sugar, a standard solution of the latter was made up, as follows: A quantity of pure sucrose (rock-candy) was pulverized and dried in the oven. 2.5 grams of this material were dissolved in 50 cc. of water and inverted according to the method of Clerget.¹ The solution was cooled, the excess of acid carefully neutralized with dilute sodium hydroxide solution, and the volume made up to 250 cc. One cc. of this solution contained, therefore, the equivalent of 0.01 gram sucrose or 0.010526 gram invert sugar. Several portions of this solution were measured out from a burette and boiled with Fehling's solution as prescribed by Allihn's method. It was found that if the mixture were allowed to stand in cold water until cool enough to weigh as usual, too high results were obtained because of a gradual deposition of cuprous oxide during the cooling. It was therefore decided to separate the precipitate from the mother-liquor as quickly as possible. After boiling for the prescribed two minutes, the mixture was poured into large test-tubes and the latter whirled in the centrifugal. The precipitate settled so quickly and so completely that the mother-liquor could be drawn off within thirty seconds from the completion of the boiling. The precipitates were then washed in the test-tubes with hot water, as described for the purification of the silver chloride precipitate. Two washings were always sufficient to leave no trace of alkali in the wash-water. The pure precipitate was then washed into the pycnometer with pure water, properly cooled, and the weight ascertained as usual. The following results were obtained:

TABLE X.—DETERMINATIONS OF INVERT SUGAR.

	Invert sugar taken. Gram.	Cuprous oxide found. Gram.	Invert sugar equivalent. Gram.	Error in milligrams.
1	0.2150	0.4026	0.2148	-0.2
2	0.1889	0.3935	0.1891	+0.2
3	0.2311	0.4311	0.2311	..
4	0.1896	0.3581	0.1890	-0.6
5	0.1595	0.3048	0.1592	-0.3

Since in this case the liquid portion of the mixture is water at a constant temperature, the only variable in the formula for calculation is α , the weight of the mixture. Hence the calculation can

¹ Bull. 46, rev. ed., Division of Chemistry, U. S. Dept. Agr., p. 39.

be much simplified by rearrangement of the formula, so as to combine all the constants of the operation into a single factor as follows:

Let c represent the weight of the pycnometer and contents.

Let c' represent the weight of the pycnometer.

Then

$$a = c - c'$$

and the formula

$$x = \frac{d(a - bd')}{d - d'}$$

becomes

$$x = \frac{d}{d - d'}(c - c' - bd') \text{ or } \frac{d}{d - d'}(c - (c' + bd')).$$

Now since Allihn's table for the dextrose equivalent of the precipitate is expressed in terms of copper instead of cuprous oxide, these results of the weighing must be divided by 1.1258, the factor for conversion of cuprous oxide into its copper equivalent. This is, of course, another constant in the calculation and may be introduced in the formula, which would then become

$$x(\text{in terms of copper}) = \frac{d}{(d - d')1.1258}(c - (c' + bd')).$$

Now the only variable in this formula is c , the weight of the pycnometer and contents. The whole expression may then be simplified as shown in the following example: In the determinations made above, the pycnometer weighed 41.7454 grams; its volume was 99.456 cc. The specific gravity of the precipitate was taken as 5.7 and of water at 20° as 0.998213. The quantity $(c' - bd')$ then became $(41.7454 + 99.456 \times 0.998213) = 141.0237$. The fraction

$$\frac{d}{(d - d')1.1258}$$

became

$$\frac{5.7}{(5.7 - 0.998213)1.1258} = 1.077.$$

The calculated amount of copper in any particular case was $(c - 141.0237)1.077$. For any other pycnometer, the value of c' and b would be different, but, once determined, they are constant and the corresponding factor may be easily calculated.

The whole process is, hence, extremely simple and may be carried out with great rapidity. After sufficient practice to

become familiar with the details of the work, a determination was easily completed in twenty minutes. While it is probable that the results are not quite so accurate as those obtained by the electrolytic estimation of the copper, they are as good as are usually required of a satisfactory method, and are subject to less variations than may easily be produced by slight changes in the conditions under which the reduction of the Fehling solution is carried out, which would affect the amount of cuprous oxide precipitated by a definite amount of reducing sugar. The method is capable of yielding more accurate results than may be obtained by the common volumetric methods for the estimation of copper, as is shown below. It possesses the added advantage that the mother-liquor is very quickly separated from the precipitate, thus diminishing the probability of the deposition of additional copper, as may happen in the case of the slower process of filtration by the other methods.

Determinations of Reducing Sugars in Commercial Glucose.—For the purpose of comparing the results obtained by this method with those obtained by the volumetric estimation of the copper, the following process was adopted. 2.25 grams of commercial glucose were dissolved in water and the volume made up to 250 cc. Aliquot portions of this solution were measured from a burette and the cuprous oxide precipitated as required by Allihn's method. The weight of cuprous oxide obtained was determined by the new method as described above; the contents of the pycnometer were then dissolved in dilute nitric acid, and the copper estimated by titration with standard potassium cyanide solution. The following results were obtained :

TABLE XI.—COMPARISON OF RESULTS OF NEW METHOD WITH CYANIDE METHOD.

Solution taken. cc.	By new method.			By potassium cyanide titration.		
	Cu ₂ O found. Gram.	Dextrose equivalent. Gram.	Dextrose per cc. Gram.	Cu ₂ O found. Gram.	Dextrose equivalent. Gram.	Dextrose per cc. Gram.
25.0	0.4078	0.2175	0.00870	0.4078	0.2175	0.00870
27.5	0.4476	0.2407	0.00875	0.4389	0.2357	0.00857
22.5	0.3723	0.1969	0.00875	0.3693	0.1953	0.00868
25.0	0.4089	0.2181	0.00872	0.4120	0.2199	0.00879

The potassium cyanide titration of copper has been in use in this laboratory for several years. The end reaction is somewhat difficult to detect, but with some experience in its use and proper

care in manipulation it has been found to give the most satisfactory results of any of the volumetric methods which have yet been tried. The determinations recorded above show that more concordant results may be obtained by the new method of weighing the precipitate than by the cyanide method of volumetric estimation.

Determination of Aluminum as Aluminum Hydroxide.—An attempt to apply this method of weighing to the aluminum hydroxide precipitate was made. The preliminary determinations of the specific gravity of the precipitate showed that the composition of the latter is not constant but varies with the time which elapses between the precipitation and the subsequent weighing of the precipitate. Considerable data bearing upon the rate of this change in composition has been accumulated and will be published at some later time. The work has proceeded far enough to show that it is probable that this method may be applied to the weighing of the aluminum hydroxide precipitate if proper conditions as to time, temperature, etc., are observed. Just what the most favorable conditions are, however, is not yet definitely determined.

CONCLUSIONS.

The work of investigating the applicability of this new method to the practices of technical analysis, is by no means complete. In fact, it is but just begun. Yet the results already obtained, which are embodied in this paper, seem sufficient to justify the belief that its application to the processes of gravimetric analysis will be a decided advance toward the much desired simplicity and ease of manipulation. They show that the use of this process greatly reduces the time required for a determination and at the same time yields very satisfactory results. A comparison of this method with the older ones when applied to the analysis of impure or mixed materials is yet to be made, but since many of the precipitates already experimented upon were weighed in the presence of solutions containing several other compounds, it is thought that the working conditions of these determinations very closely approximate those of ordinary analyses. The results already obtained, therefore, lead to the conclusion that the proposed method is a step toward the realization of the conditions of an ideal method of analysis, namely, accuracy and rapidity.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY
No. 60.]

THE ELECTROLYTIC DETERMINATION OF MOLYBDENUM.

BY LILY GAVIT KOLLOCK AND EDGAR F. SMITH.

Received July 5, 1901.

MORE than twenty years ago Smith,¹ in describing his experience in the electrolysis of solutions of ammonium molybdate, wrote: "The deposition, although complete, was so very slow that this method of determination was practically of little value." During the last few months attention has again been given in this laboratory to the subject. Sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) was dissolved so that 0.1302 gram of molybdenum trioxide was present in 125 cc. of solution, which was exposed for several hours to the action of a current of 0.1 ampere and 4 volts. The temperature of the electrolyte was 75° C. No precipitation occurred upon either electrode. Upon adding two drops of concentrated sulphuric acid to the liquid, it at once assumed a dark blue color. As the current continued to act, this color disappeared and the cathode was coated with a black deposit—the hydrated sesquioxide.² On removing the colorless liquid and testing it with ammonium thiocyanide, zinc, and hydrochloric acid, evidences of the presence of molybdenum failed to appear. In the following experiments the molybdenum deposit was a brilliant black in color and so adherent that it could be washed without detaching any particles. Usually the colorless liquid was removed with a siphon, cold water being introduced without interrupting the current. The deposit was not dried, but while yet moist it was dissolved from off the dish in dilute nitric acid and the solution carefully evaporated to dryness, the residue being heated upon an iron plate to expel the final traces of acid. White molybdic acid remained. It was noticed several times that blue spots existed here and there in the mass, but these were removed by moistening the residue with nitric acid and evaporating a second time to dryness. This procedure was adopted in all the trials given below. Concordant results could not be obtained by merely drying the hydrate at a definite temperature. The same was true also on attempting to ignite the hydrate to trioxide. Loss then occurred from sublimation and volatilization.

¹ *Am. Chem. J.*, 1, 337.

² *Ibid.*, 1, 338.

RESULTS.

	Molybdenum trioxide pre- sent in grams.	Sulphuric acid added. cc.	Dilution.	Temperature. °C.	Current.	Voltage.	Time. Hours.	Molybdenum trioxide found in grams.	Error in grams.
1	0.1302	0.1	125	70	N.D. ₁₀₇ = 0.022 A	2.0	4 $\frac{1}{2}$	0.1299	- 0.0003
2	0.1302	0.1	125	80	N.D. ₁₀₇ = 0.045 A	2.25	2 $\frac{1}{2}$	0.1302	...
3	0.1302	0.1	125	70	N.D. ₁₀₇ = 0.04 A	2.2	4 $\frac{1}{2}$	0.1302	...
4	0.2604	0.2	125	75	N.D. ₁₀₇ = 0.04 A	2.0	7	0.2603	- 0.0001
5	0.1541	0.2	125	85	N.D. ₁₀₇ = 0.04 A	1.9	2 $\frac{1}{2}$	0.1541	...
6	0.1541	0.2	125	80	N.D. ₁₀₇ = 0.035 A	2.1	4	0.1540	- 0.0001

The method is accurate, is easy of execution, and, as will be observed, requires comparatively little time. There seems to be no apparent reason why it should not replace some of the older and less reliable methods pursued in the determination of this element.

One of the first directions in which it seemed that the method could be made useful, was in the determination of the molybdenum content of the mineral molybdenite. By fusing the latter with a mixture of pure alkaline carbonate and nitrate, sodium molybdate and sulphate would be formed. If the sulphur was not to be determined, after dissolving out the fusion with water, and filtering out the insoluble oxides, it would only be necessary to acidulate the alkaline liquid with dilute sulphuric acid and proceed with the electrolysis; but in cases where an estimation of the sulphur was desired, it was thought that acetic acid would answer for the purpose of acidulation. To ascertain the latter fact the experiments given below were instituted. The solution, acidified with this acid, did not acquire a blue color on passing the current through it. The deposit of hydrated oxide was very adherent and was readily washed. It will, however, be noticed that a longer time is necessary for the complete precipitation. It is also advisable not to add the entire volume of acetic acid at first, but to introduce it gradually from time to time, from a burette.

RESULTS.

	Molybdenum trioxide pre- sent in grams.	Acetic acid added. cc.	Dilution.	Temperature. °C.	Current.	Voltage.	Time. Hours.	Molybdenum trioxide found in grams.	Error in grams.
1	0.1541	1	125	85	N.D. ₁₀₇ = 0.075 A	4.4	7 $\frac{1}{2}$	0.1541	...
2	0.1541	1	125	85	N.D. ₁₀₇ = 0.075 A	4.4	3	0.1540	- 0.0001
3	0.1541	1	125	80	N.D. ₁₀₇ = 0.05 A	2.5	6	0.1543	+ 0.0002

In the last experiment, 5 grams of sodium acetate were added in order to increase the conductivity of the solution and also to ascertain what effect an excess of this salt would have, because, if the acetic acid were used to acidify the alkaline solution obtained by the decomposition of molybdenite, a great deal of this salt would be present. The concordant results justified the next step, which was to decompose weighed amounts of pulverized molybdenite with sodium carbonate and nitrate, then take up the fusion with water, filter out the insoluble oxides, acidify with acetic acid, boil off the carbon dioxide, and electrolyze. The liquid poured off from the deposit of the sesquihydroxide was heated to boiling and precipitated with a hot solution of barium chloride.

RESULTS OBTAINED FROM MOYBDENITE.

	Molybdenite in grams.	Molybdenum found in per cent.	Sulphur found in per cent.
1	0.2869	57.37	38.28
2	0.1005	57.15	38.33
3	0.1388	56.83	37.87

MOLYBDENUM-SULPHUR RATIO.

(1).....	I : 2.004
(2).....	I : 2.012
(3).....	I : 1.998

From several experiments, which will not be recorded here, there is a possibility of separating molybdenum electrolytically from tungsten, the latter, of course, being present as an alkaline tungstate. Further work, however, will be necessary to fully establish this hope.

The experience detailed above proves conclusively that molybdenum must also be included in the list of metals which can be determined with the aid of the current and the analysis of molybdenite, as outlined, is vastly better than the usual procedures.

UNIVERSITY OF PENNSYLVANIA.

A COMPARISON OF THE SOLUBILITY OF ACETYLENE AND ETHYLENE.

BY SAMUEL AUCHMUTY TUCKER AND HERBERT R. MOODY.

Received June 12, 1901.

NO satisfactory or convenient method for the separation of acetylene and ethylene has yet been devised. The two gases exhibit such a similarity in their solubility that very few

reagents are known which will make a quantitative separation. The necessity for this separation arose while the authors were preparing ethylene which was generated simultaneously with acetylene from certain products produced in the electric furnace.

The reagents known to be good solvents for acetylene are water, ammoniacal or acid cuprous chloride, ammoniacal silver chloride or the nitrate, acetone, and alcohol ; and those commonly mentioned as dissolving ethylene are bromine and sulphuric acid.

Wherever any mention is made of a separation of acetylene and ethylene it is generally taken for granted that the latter gas is completely insoluble in ammoniacal cuprous chloride, and the analysis is based upon this false assumption, Hempel being the one authority who takes a different view. The method suggested by him for the determination of acetylene although accurate was found undesirable owing to the length of time it takes for the analysis. This method is not recommended by the author for the separation of the two gases but merely as a means of determining acetylene. However, owing to the fact (stated later) that ethylene dissolves in cuprous chloride to form a soluble compound, this method is applicable to the separation of the two gases.

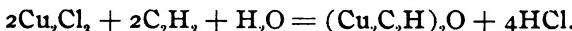
The method as used by us was carried out as follows : The cuprous chloride was contained in a train of five 5-inch U-tubes containing about 20 cc. each of the absorbent. To prevent the mechanical lifting of the precipitate into the connecting tubes, it was found desirable to use U-tubes with bulbs blown on each limb.

The mixed gases were collected over mercury in a pair of ordinary Hempel burettes, and from these delivered very slowly through the train of tubes. After all the gas was delivered from the burette, a T opening into the delivery tube was used for the introduction of nitrogen or hydrogen gas which acted as a sweep.

The red precipitate which was found in the tubes corresponds to $(\text{Cu}_2\text{C}_2\text{H})_2\text{O}$. This was removed from the tubes, collected on a filter, washed to remove soluble copper compounds, dissolved in hydrochloric acid, converted to sulphate, and the copper deposited electrolytically. The quantity of acetylene in the original gas is easily calculated from this weight of copper. This method was tried repeatedly with good results, the only source of error being the possibility of loss through too rapid passage of the gas, and the only objection the amount of time consumed. In fact it is out of the question to make a rapid separation of the gases by

this method. Consequently an attempt was made to find a reagent which would absorb the acetylene and leave the ethylene undissolved.

The solvent action on ethylene of known absorbents of acetylene was first determined. The usual solvent recommended for acetylene is ammoniacal cuprous chloride. This solution is made up of 42 grams cupric chloride, 32 grams copper turnings, 100 cc. hot water, and 200 cc. commercial hydrochloric acid. The mixture is boiled for two or three hours and then a little concentrated hydrochloric acid added, and the whole boiled until it is pale yellow. This was cooled and an excess of ammonium hydroxide added. Such a solution was found to absorb acetylene rapidly and completely according to the following reaction:¹



The next step was to investigate the solubility of known ethylene, this gas being generated by the action of metallic zinc on ethylene dibromide. Ethylene is so little soluble in water that there was no trouble to apprehend from such a small amount being absorbed. This was found by actual trial, and also the solubility in ammonium hydroxide. Here again a very slight solubility was noticed. Considering these two facts and that ethylene is not usually considered to be soluble in cuprous chloride, it seemed surprising, when either ammoniacal or acid cuprous chloride was added to a sample of ethylene to find that fully 95 per cent. of the gas was absorbed.

The foregoing is apparently not taken into account by Moissan whose results, according to the method of procedure given on pages 313 and 320 of "Le Four Électrique," can hardly be right. To be sure, the method is only spoken of in a vague way, but as stated in the reference given, it is natural to suppose that ethylene was considered as insoluble in the copper salt. If this were the fact, a large portion of the ethylene evolved from his thorium carbide must have been absorbed with the acetylene and counted with the latter.

Thinking that a mixture of ethylene and acetylene might act differently from either taken alone, equal volumes of the two gases were mixed and nearly the total volume was found to be absorbed by the copper solution. Other good solvents for acetylene are alcohol (1 volume of alcohol dissolves 6 volumes acety-

¹ Hempel's "Gas Analysis," p. 183.

lene) and acetone (1 volume of acetone dissolves 25 volumes acetylene). To investigate the possibilities of using either of these to absorb the acetylene and leave the ethylene the solubility of the latter gas was tried. Thirty cc. of pure ethylene were found to be all absorbed by acetone. Similarly when 100 cc. of ethylene were treated with an excess of 95 per cent. ethyl alcohol, a residue of less than 10 cc. was left, showing that both reagents were worthless for the purpose.

Since Nordhausen acid is such a good absorbent for ethylene, it seemed possible that it might first remove the ethylene and leave the acetylene. To determine this 56 cc. of known pure acetylene were passed several times into a Hempel pipette filled with the acid, and after two passages, over 60 per cent. of the acetylene was absorbed, showing that the reagent also failed in the required purpose. Finally the action of ammoniacal silver was investigated with the following results : The solution was made up by dissolving 10 grams silver nitrate in 500 cc. of water, making the solution barely acid with hydrochloric acid and then slightly ammoniacal. The clear solution thus obtained proved to be an excellent solvent for acetylene although it is slower in its action than ammoniacal cuprous chloride. The compound formed by its action is, according to Lewes,¹ Ag_2C , and not $\text{C}_2\text{H}_2\text{Ag}_2\text{O}$ as stated by other authorities.

It now remained to try its action upon ethylene. When 26 cc. of known ethylene were treated with an excess of ammoniacal silver chloride, only 0.2 cc. were absorbed, and repeated trials gave the same result ; so that, although there is not absolute insolubility of ethylene, the method was admirable for its quickness and, of course, infinitely more accurate than the use of ammoniacal cuprous chloride.

Lastly the effect of the reagent upon known mixtures of pure acetylene and ethylene was tried. 29.2 cc. of ethylene and 37.3 cc. of acetylene were taken, and treated with the silver solution. The residue left corresponded closely with the volume of ethylene taken, thus showing conclusively that a mixture of the two gases may readily be separated by this method. Fractional percentages of ethylene might be lost and for such small amounts there seems nothing better than recourse to the gravimetric determination of the copper corresponding to the acetylene present, but this is not necessary for ordinary work.

¹ Lewes' "Acetylene," p. 154.

THE DETERMINATION OF SULPHUR IN IRON AND STEEL.

BY WILLIAM A. NOYES AND L. LESLIE HELMER.¹

Received July 1, 1901.

ALTHOUGH very many methods for the determination of sulphur in iron have been proposed,² none of those in common use is altogether satisfactory. None of the evolution methods will give correct results with some irons, unless the evolved gases are led through a heated tube to convert organic compounds of sulphur into hydrogen sulphide.³ The aqua regia method sometimes leaves sulphur in the residue⁴ and the precipitation of barium sulphate in the presence of iron, which it usually involves, is always objectionable. The method which we propose obviates at least a part of these difficulties.

SOLUTION.

We tried at first various methods of solution, including solution in concentrated nitric acid and hydrochloric acid, as given by Blair in his "Chemical Analysis of Iron," in concentrated nitric acid with a little potassium chlorate toward the end of the solution; in hydrochloric acid and potassium chlorate; in bromine and water; and in dilute nitric acid with a little potassium bromide and an excess of potassium chlorate. The last two methods were finally adopted as the most satisfactory.

Solution in Bromine and Water.—The bromine must, of course, be free from sulphur. Ours was purified by mixing with a little dry sodium carbonate and distilling from a plain retort. Put 200 cc. of water and 8 cc. of bromine in a flask and add 5 grams of the iron or steel in portions, cooling after each addition. Solution takes place readily. When it is complete, boil for a moment to expel the slight excess of bromine. Filter, wash the residue, add to it some sodium carbonate and burn the filter in a platinum crucible, using an alcohol lamp, and completing the oxidation by the addition of some potassium nitrate. Dissolve the residue in water, filter, acidify with hydrochloric acid, add 5 cc. of barium chloride solution, digest till the precipitate settles readily and

¹ The work here described formed the basis of a thesis for the degree of Bachelor of Science at the Rose Polytechnic Institute. The preliminary work on the subject was done by Mr. Herbert F. Madison, of the class of 1900.

² See Bibliography by Brearley in *Chem. News*, 82, 281 (1900).

³ Phillips: This Journal, 17, 891.

⁴ Blair: This Journal, 19, 114.

determine as usual.¹ Add *three-fifths* of the weight of barium sulphate found here to that obtained from the main solution. The main solution, containing ferric bromide, is to be precipitated as described below.

More sulphur is usually found in the residue by this process than by the solution in nitric acid and potassium chlorate, but it has the advantage that the solution can be filtered at once, while the solution in nitric acid clogs a filter so badly that evaporation to dryness is required.

2. Solution in Nitric Acid, Potassium Bromide and Potassium Chlorate.—Put into a flask 120 cc. of dilute nitric acid (sp. gr. 1.20, or 1:2 by volume) and 1 gram of potassium bromide. Add in portions, 5 grams of the iron mixed with 7 grams of potassium chlorate, cooling somewhat, if necessary. When the iron is dissolved, transfer to a flat porcelain dish and evaporate to dryness in such a manner that contact with the products of combustion of the gas is avoided. Dissolve the residue in concentrated hydrochloric acid, dilute, filter, and treat the residue as before, and the filtrate as directed below.

PRECIPITATION.

Put into a 500 cc. graduated flask 130 cc. of ammonia (10 per cent.), and add the solution obtained by either method above. Make the volume up to 500 cc., mix thoroughly by pouring back and forth into a dry beaker, and filter through a dry filter. The filtrate must, of course, be strongly alkaline. Take 300 cc. of the filtrate and evaporate, in a wide beaker, to 100 cc. During this evaporation contact with the products of combustion of illuminating gas must be avoided. We have used for the purpose a piece of stove-pipe flattened on one side and connected at one end with an elbow and upright piece to carry away the products of combustion. The hot steam plate of most iron and steel laboratories would be admirably adapted to this purpose. Add one drop of dilute hydrochloric acid (sp. gr. 1.12) and 10 cc. of barium chloride, digest hot till the precipitate settles quickly after stirring; filter, ignite and weigh as usual. The precipitate represents the amount of sulphur in 3 grams of the iron or steel.

To test the accuracy of the precipitation, seven determinations

¹ Dr. C. B. Dudley, who has kindly done some work with the bromine method, is of the opinion that the barium sulphate obtained from the residue requires purification by fusion with sodium carbonate, and it seems that this point requires further study.

were made with solutions containing known amounts of sulphur. For the first three a low sulphur steel was dissolved in hydrochloric acid, the solution boiled, filtered, and oxidized to ferric iron with bromine. Two blanks, made with quantities of this solution representing 5 grams of iron, gave respectively 0.0001 and 0.0004 gram barium sulphate.

The fourth and fifth determinations were made with a solution obtained by dissolving 5 grams of steel No. 1 in water and bromine. The mean value for the sulphur in this steel, neglecting the residue, had been found to be 0.027 per cent. The sixth and seventh determinations were made with 5 grams of iron No. 1, which contains, apart from the residue, 0.095 per cent. of sulphur. The extra sulphur for these experiments was added in the form of ferrous ammonium sulphate. The results are stated as percentages of the iron used, and indicate the accuracy to be expected in actual work, so far as this depends on the method of precipitation used.

Sample.	Sulphur present.	Sulphur found.
Sulphur-free iron + $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$,.....	0.0056	0.0050
Sulphur-free iron + $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$,.....	0.012	0.011
Sulphur-free iron + $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$,.....	0.016	0.016
Steel No. 1 + $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$,.....	0.129	0.129
Steel No. 1 + $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$,.....	0.234	0.211
Iron No. 1 + $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$,.....	0.490	0.500
Iron No. 1 + $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$,.....	0.689	0.679

The advantages of this method of precipitation are that the precipitation is made with a solution free from iron, and that by the evaporation of the ammoniacal solution it becomes neutral, and by the addition of one drop of dilute hydrochloric acid a constant degree of acidity is secured. The results indicate that, even with very small amounts of sulphur, an accurate precipitation is secured in the presence of ammonium chloride or bromide.

To secure a uniform sample for use in testing the method, a considerable quantity of cast-iron drillings were ground to a fine powder in a heavy iron mill. Samples Nos. 1 and 2 were prepared in this way. Samples Nos. 3, 4, and 5 were ordinary drillings of iron used in making car wheels. Nos. 6 and 7 were samples of steel.

Determinations were made with sample No. 1 by Blair's gravimetric evolution method, using an alkaline solution of lead to

absorb the hydrogen sulphide evolved; and by Blair's aqua regia method, precipitating the sulphuric acid in the presence of the iron. As will be seen below, the evolution method gives less than one-half of the sulphur actually present in this iron. Whether the irregular and low results obtained by the aqua regia method are due to a failure to secure a complete oxidation of the sulphur during solution, or to imperfect precipitation of barium sulphate in the acid iron solution, can not be known with certainty, but the results of the aqua regia method, combined with our method of precipitation, point rather to the first explanation as the true one. The following are the results with iron No. I.:

Evolution method, Blair.	Aqua regia method, Blair.	
0.044	0.084	0.077
0.049	0.080	0.068
0.044	0.088	0.058
0.042

The following determinations were made with different methods of solution followed by precipitation of the iron with ammonia and determination of the sulphuric acid in an aliquot part of the filtrate.

Sample.	100 cc. H ₂ O, 35 cc. HCl (1.12), 7 grams KClO ₃ .	Con. HNO ₃ with little con. HCl, Blair.	40 cc. con. HNO ₃ with 1/2 gram KClO ₃ .	100 cc. HNO ₃ (1.20), 7 grams KClO ₃ .	200 cc. H ₂ O, 8 cc. Br.
Iron No. I.	0.105	0.059	0.094	0.075	0.097
Iron No. I.	0.041	0.074	0.097	0.084	0.095
Iron No. I.	0.079	0.098	0.089	0.088	0.095
Iron No. I.	0.077	0.031	0.087
Iron No. I.	0.054	0.090

The results indicate that the use of concentrated nitric acid with the addition of a little potassium chlorate, when solution is nearly complete, or the use of bromine and water, give the most concordant and, probably, the most accurate results. The first of these methods is accompanied by the evolution of large volumes of nitrogen peroxide and requires considerable time. Solution in dilute nitric acid (sp. gr. 1.20) with potassium bromide and 7 grams of potassium chlorate is more rapid and gives satisfactory results.

In the following determinations the methods which have been described in detail were used. When the total sulphur is not given the solution was poured into the ammonia without previous

filtration. Where the total sulphur is given, the solution in bromine was filtered and the sulphur in the residue determined, while the solution in nitric acid was evaporated to dryness, the residue dissolved in concentrated hydrochloric acid, diluted, filtered, and the sulphur in the residue determined.

Sample.	200 cc. H ₂ O, 8 cc. Br.		120 cc. HNO ₃ (1.20), 1 gram KBr, 7 grams KClO ₃ .	
	Soluble sulphur.	Total sulphur.	Soluble sulphur.	Total sulphur.
Iron No. 1.	0.097	0.084
Iron No. 1.	0.095	0.088
Iron No. 1.	0.095	..	0.091
Iron No. 1.	0.085	0.106	0.088
Iron No. 1.	0.093	0.117	0.093	0.120
Iron No. 1.	0.083	0.106
Iron No. 1.	0.099	0.116
Iron No. 1.	0.095	0.107
Iron No. 2.	0.068	0.091	0.088	0.099
Iron No. 2.	0.070	0.092	0.086	0.095
Iron No. 3.	0.129	0.155	0.157	0.159
Iron No. 3.	0.129	0.148	0.155	0.159
Iron No. 4.	0.113	0.144	0.142	0.149
Iron No. 4.	0.110	0.147	0.141	0.149
Iron No. 5.	0.075	0.095	0.083	0.095
Iron No. 5.	0.077	0.094	0.079	0.089
Steel No. 6.	0.026
Steel No. 6.	0.027
Steel No. 6.	0.026
Steel No. 6.	0.029
Steel No. 7.	0.018	0.029	0.019	0.022
Steel No. 7.	0.017	0.025	0.014	0.025

The sulphur of the residue, after solution in bromine and water, varies from 0.015 to 0.037 per cent. with an average of 0.023. The sulphur in the residue after solution in nitric acid, potassium bromide, and potassium chlorate, and evaporation, varies from 0.002 to 0.027 per cent. with an average of 0.012. With iron of a given character, the sulphur in the residue will probably be found nearly uniform, so that the original solution can be precipitated at once with ammonia, without previous filtration, and a constant correction for the sulphur of the residue applied. When this is done, the method becomes, we think, more rapid than any gravimetric method now in use.

TERRE HAUTE,
June 28, 1901.

THE SULPHOHALIDES OF LEAD.

By VICTOR LENHER.

Received June 19, 1901.

WHEN hydrogen sulphide is allowed to come in contact with a solution of lead chloride in hydrochloric acid, a brick-red precipitate appears. This precipitate consists of a combination of lead sulphide with the chloride. Hünefeld¹ prepared and studied this red substance and ascribed to it the formula $3\text{PbS}.2\text{PbCl}_2$. He treated a dilute lead acetate solution with hydrochloric acid and added hydrogen sulphide to the solution.

Reimsch² later studied the same substance. Parmentier³ considers the formula $\text{PbS}.\text{PbCl}_2$ more nearly correct as it would be analogous to the oxychloride, $\text{PbO}.\text{PbCl}_2$.

It is also possible to prepare a yellowish red sulphochloride by digesting freshly precipitated lead sulphide with a solution of lead chloride.

Lead sulphochloride is a rather unstable body. Hot water gradually extracts lead chloride from it, leaving the sulphide. Excess of hydrogen sulphide completely converts it into the pure black sulphide.

Lead bromosulphide, like the chlorosulphide, is brick-red in color. Parmentier, who first obtained it, states that it can be prepared more readily than the chlorosulphide, but it is similar in its properties to the chlorosulphide. It corresponds to the formula $\text{PbS}.\text{PbBr}_2$.

Various attempts had been made to prepare the analogous iodosulphide of lead, but on account of the insolubility of lead iodide in dilute hydriodic acid, the attempts were fruitless until the author⁴ tried the action of a solution of hydrogen sulphide on a solution of lead iodide in potassium iodide. This method of procedure gives the lead iodosulphide brick-red in color, having a more yellow shade than the other sulphohalides but similar in all respects to these derivatives. This brick-red lead iodosulphide corresponds to the formula $\text{PbS}.4\text{PbI}_2$. It is a very unstable compound.

¹ *J. prakt. Chem.*, **7**, 27.

² *Ibid.*, **13**, 130.

³ *Compt. rend.*, **114**, 298.

⁴ This Journal, **17**, 511.

While lead iodide is almost insoluble in dilute hydriodic acid, it dissolves readily in the stronger acid. When hydrogen sulphide gas is added to a solution of lead iodide in hydriodic acid, neither the sulphide nor the iodosulphide is obtained. If, however, an aqueous solution of hydrogen sulphide is added to the hydriodic acid solution of the iodide, yellow lead iodide is first precipitated by the dilution and appears as a fine crystalline precipitate. Further addition of hydrogen sulphide solution causes the conversion of the yellow iodide into the brick-red iodosulphide. This precipitate on analysis was found to correspond to the formula $PbS \cdot 4PbI_2$. We are therefore led to believe that whatever the method of preparation, the red iodosulphide of lead has always the same composition.

Thus far it has been impossible to obtain a lead fluorsulphide. The slight solubility of lead fluoride in water, and in the alkaline fluorides has thus far prevented its preparation. It has likewise been impossible to obtain a fluorsulphide by digesting lead fluoride with lead sulphide in a similar manner to that by which it is possible to prepare the chlorosulphide. Moreover, lead sulphide is insoluble in hydrofluoric acid while the other halogen acids readily dissolve the sulphide. Its preparation would appear improbable.

That these derivatives are possible under certain definite conditions and that these conditions must be adhered to, is evidenced by the fact that a too dilute solution of the lead salt in the halogen acid, or even a slight excess of hydrogen sulphide, causes the formation of pure black lead sulphide, which contains no halogen. On the other hand, since lead sulphide is soluble in the strong aqueous solutions of the halogen acids, it is impossible to prepare these compounds by means of the addition of hydrogen sulphide to the strong acid solutions. It is necessary that certain conditions be observed in order to make the existence of these compounds possible.

That such conditions are necessary can be shown in a very simple manner. Either precipitated lead sulphide or the natural sulphide, galena, dissolves readily in the strong aqueous halogen acids with evolution of hydrogen sulphide gas and the formation of the corresponding halide. With a strong halogen acid, hydrogen sulphide is liberated and when sufficient liquid is present, part of the gas remains in solution. The addition of water to

this solution gives, when proper conditions are established, the brick-red compound which might be considered as an intermediate product between the halide and the sulphide.

The three sulphohalides of lead are all readily prepared by this means. The bromosulphide is the most stable of the compounds and it can be prepared in a very striking manner by treating 2 to 3 grams of lead sulphide or galena with 10 to 15 cc. of strong hydrobromic acid, and diluting with a large volume of water. The acid should be allowed to act until hydrogen sulphide is freely evolved. The solution will retain sufficient gas so that when a liter of water is quickly added, the brick-red bromosulphide appears.

Hydrochloric and hydriodic acid solutions of galena, when freshly prepared and quickly diluted, behave in a similar manner. With the hydrochloric acid solution the conditions are better obtained when more acid is present than above noted for hydrobromic. When this solution is diluted with water, the bright red chlorosulphide appears, sometimes preceded by the white chloride. Excess of water invariably causes the chlorosulphide to change to the black lead sulphide, which is the final product. The formation of the bromosulphide by this method makes an extremely beautiful experiment; the simple addition of water to a freshly prepared solution of galena in hydrobromic acid gives bright yellow bromide which almost instantly changes to a bright red. On further diluting and allowing to stand, the black sulphide is obtained. These changes seem to indicate that the formation of these compounds is due to certain definite relations between the halide and hydrogen sulphide in a solution of the corresponding halogen acid.

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A MODIFICATION OF THE SULPHURIC ACID TEST FOR FORMALDEHYDE IN MILK.

BY A. GUSTAV LUEBERT.

Received July 10, 1901.

WHILE estimating nitrogen, by the Kjeldahl-Gunning method, in a number of samples of milk which had been preserved by the addition of a small quantity of formaldehyde, a peculiar violet coloration of the potassium sulphate crystals and sulphuric acid, surrounding them, was noticed. Especially was

this true when the milk was added to the potassium sulphate and the sulphuric acid carefully poured down the side of the digestion flask, so that the liquids did not immediately mix. The violet or reddish-violet color appeared only in those samples of milk which contained the formaldehyde; in all others caramelization ensued at once, the crystals and the liquid becoming first brown and then black.

A number of tests were made upon milk to which formaldehyde had been added, and in each case the preservative seemed to retard the oxidizing action of sulphuric acid, causing the violet coloration to appear and preventing the usual caramelization of the milk. In none of the samples where formaldehyde was added was a negative result obtained.

These trials led to the adoption of the following method for the detection of formaldehyde in samples of milk: 5 grams of coarsely powdered potassium sulphate are placed in a 100 cc. flask, 5 cc. of the suspected milk distributed over it by means of a pipette and 10 cc. of sulphuric acid (sp. gr. 1.84), carefully poured down the side of the flask. It is now allowed to stand quietly until the color develops. If formaldehyde is present the violet coloration of the potassium sulphate takes place in a few minutes, the color gradually dispersing through the entire liquid. If no formaldehyde be present the liquid will at once assume a brown color, rapidly changing to black. Milk which has stood for several hours previous to testing gives the reaction even more rapidly than a fresh sample.

This test is sensitive to a dilution of at least one part formaldehyde in 250,000 parts of milk.

NEW BOOKS.

QUALITATIVE ANALYSIS: A GUIDE IN QUALITATIVE WORK, WITH DATA FOR ANALYTICAL OPERATIONS AND LABORATORY METHODS IN INORGANIC CHEMISTRY. BY ALBERT B. PRESCOTT AND OTIS C. JOHNSON. Fifth Revised and Enlarged Edition, Entirely Rewritten. New York: D. Van Nostrand Co. 1901. xi + 420 pp. Price, \$3.50.

So much new matter has been added to this edition of Prescott and Johnson's manual that it is almost a new work. The subject matter has been enlarged over the former edition by fully one-half, and the size of the book increased 100 pages. The introduction of a section on "Solution and Ionization" will aid teachers in making the subject clear to beginners. Much descriptive

chemistry has been introduced throughout the book, and while at first sight this may seem a little foreign to a work of this class, it must be remembered that not only will this serve the student as a review of elementary chemistry, but the knowledge given of the physical properties, such as the color and solubility of the various salts, will greatly aid him in forming his opinion as to the composition of a substance. The descriptive, as well as the analytical, matter is well arranged under a series of systematic headings, and the former is separated from the latter by the use of small type. Reactions are used throughout the book to show the changes that take place in precipitation, solution, etc., and the schemes and tables are carefully explained. The rare elements receive their share of attention, and the book is brought well up to date in the introduction of new tests. Abundant reference to the literature of chemistry makes it easy for those so inclined to go deeper into any part of the subject. The book is well printed and neatly bound. In the reviewer's opinion the manual is the most complete work on the subject printed in English, and it deserves to rank with the standard German manual of Fresenius. Whether the teacher can use it in the classroom is for each individual to decide for himself, but the book should certainly be in the library of every teacher of chemistry, and may well be in that of every professional chemist and student of chemistry.

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THE QUANTITATIVE SEPARATION AND DETERMINA-TION OF URANIUM.

BY EDWARD F. KERN.

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THE work described in this article was undertaken with the object of finding out the most accurate and satisfactory method for the technical estimation of uranium.

The usual quantitative methods for the estimation of uranium were first repeated, then new methods for its separation and estimation were tried on solutions containing known amounts of pure salts, and the best conditions for both separation and determination were carefully worked out.

The research was drawn to a close by making a number of assays of uraninite, in which the results obtained from the work on pure salt solutions were applied. These assays tested the methods on the most important ore of uranium, and thus collected the data in the form of analytical methods.

HISTORICAL INTRODUCTION.

Uranium was discovered by M. H. Klaproth, who separated what he thought to be a new element from pitchblende—also known as uraninite—the principal ore of uranium. This was in

1789, and what he obtained was not the element, but its lower oxide, UO_2 . He named the element uranium in remembrance of the planet Uranus, which Herschel discovered in 1781.

From 1789 to 1795 much work was done on the investigation of uranium, but nothing new was discovered till 1840, when E. Péligot succeeded in isolating metallic uranium in powder form by heating uranous chloride (UCl_4) with metallic sodium.¹ He made a great number of experiments, the results of which proved that what was previously thought to be the element uranium was its lower oxide (UO_2), which plays the part of a base, a true inorganic radical. This discovery seems to have been an impetus to the further study of this element, as we find records in the different journals, of the years that follow, of several of the eminent chemists of the day investigating uranium and trying to find new methods for its estimation.

Clemens Zimmerman was the next chemist of note to investigate uranium. He studied methods for isolating the metal, and methods for its estimation and separation from other elements, and prepared many of its salts, studying their chemical and physical properties.² This work covered a number of years, from 1877 to 1884. So 1877 marks the second revival of interest in the element uranium. The first revival was in 1840, when Péligot isolated metallic uranium. The third revival is the present time, brought on by the great industrial demand for uranium ores.

In 1854 the only use to which uranium was put was for making a very fine black for porcelain painting,³ and from 1850 to 1866 it was much used in photography. At present its uses are for the preparation of acetate and nitrate salts (which are used as chemical reagents), for the manufacture of a certain highly prized canary-yellow colored glass, for the preparation of a pigment used for porcelain painting, and lastly for making a steel which has properties superior to nickel steel.⁴

PART I.—SEPARATION OF URANIUM.

SEPARATION OF URANIUM FROM MEMBERS OF THE FIFTH AND SIXTH GROUPS.

The only point to be determined for the well-known separation

¹ *Ann. Chem.* (Liebig), 41, 141 (1842).

² *Ibid.*, Vols. 119, 204, 213 and 214.

³ Whitney's "Mineral Wealth of the United States."

⁴ *Moniteur Industrial*, 27, 44 (1900).

by hydrogen sulphide was the exact acidity of the solution. This was done by mixing standardized solutions of lead, copper, and uranium in different proportions, and precipitating the lead and copper by hydrogen sulphide, under varying conditions of acidity and temperature. The experiments were all conducted quantitatively. These showed that a perfect separation was effected when 1 cc. of concentrated nitric acid (sp. gr. 1.42) was present to every 50 cc. of solution, and the solution saturated with hydrogen sulphide in the cold.

With hydrochloric acid, 1 cc. of concentrated acid (sp. gr. 1.20) to 50 cc. of solution gave excellent results. This amount must not be exceeded, as when 2.5 per cent. of concentrated acid was present the precipitation of the lead was incomplete. Less acid must be present if the precipitation is done from a hot solution, but this is not recommended.

As 5 cc. of concentrated acid in a bulk of 250 cc. solution gave a perfect separation of uranium from the metals of the fifth group, whose sulphides are the most soluble—lead and cadmium—and also from copper, these conditions must also be suitable for the other members of this group. Lead requires the least amount of free acid to retain it in solution; then follow in order of succession, cadmium, mercury, bismuth, copper, and silver.¹

SEPARATION OF VANADIUM FROM URANIUM.

Vanadium is one of the common associates of uranium, and especially so in the minerals which occur in Colorado. Carnotite, the most common of these minerals, has of late reached commercial importance.

The separation of vanadium from uranium presents very little difficulty unless phosphoric acid is present, in which case the separation is troublesome. Friedel and Cumenge² separated vanadium from uranium by evaporating the solution to dryness with nitric acid. The uranium was then extracted from the dry mass with a warm dilute solution of ammonium nitrate. For this separation, no phosphoric acid should be present as it renders the uranium oxide, with which it is combined, insoluble in the dilute ammonium nitrate solution.

The method for the separation of vanadium from iron by means

¹ Fresenius' "Quantitative Chemical Analysis," p. 456, 1900.

² Am. J. Sci., 10, 135 (1900).

of mercuric oxide and mercurous nitrate¹ has been used with success by A. C. Langmuir,² for the separation of vanadium from uranium in the analysis of carnotite. The finely divided mineral was dissolved in the smallest possible amount of nitric acid, and the silica filtered off. The solution was diluted to about 500 cc. and the vanadium precipitated by means of mercurous nitrate as follows: The nitric acid solution was nearly neutralized with pure yellow mercuric oxide, and the vanadium then precipitated by the addition of a strong solution of mercurous nitrate. The solution was brought to boiling, after which it was filtered. (If chromium, tungsten, or molybdenum are present they go down as mercurous salts with the mercurous vanadate.) The precipitate was washed with a warm dilute solution of mercurous nitrate, after which it was dried, ignited, and weighed as V_2O_5 . The excess of mercury in the filtrate was removed by means of hydrogen sulphide gas. After expelling the hydrogen sulphide from the filtrate by slow boiling, the uranium was determined by the ordinary method.

*O. P. Fritchie's Method*³ is said to be particularly adapted to the mineral carnotite. The finely divided mineral was decomposed at boiling temperature with 10 cc. nitric acid, taken up with 10 cc. water, neutralized with a saturated solution of sodium carbonate, added 5 cc. in excess, and 20 cc. of a 20 per cent. sodium hydroxide solution; it was boiled slowly for half an hour, and the precipitate allowed to settle. The vanadium, uranium, and iron were all precipitated by the sodium carbonate, but on adding a moderate excess and a large excess of sodium hydroxide, the vanadium was dissolved while the uranium and iron remained insoluble. Uranium is easily precipitated by sodium carbonate and sodium hydroxide in the presence of an iron salt. The precipitate was washed with a solution of sodium hydroxide. The uranium and iron were then separated by the ordinary method, and each determined volumetrically by means of standard permanganate, after reducing their sulphate solutions at boiling temperature with metallic aluminum.

SEPARATION OF URANIUM FROM MEMBERS OF THE THIRD AND FOURTH GROUPS, PARTICULARLY IRON.

The methods ordinarily used for separating uranium from the

¹ Blair's "Chemical Analysis of Iron," 3rd edition, p. 200.

² Paper read before N. Y. Section of American Chemical Society, at March meeting.

³ Eng. Min. J., Nov. 10, 1900; Chem. News, 82, 258 (1900).

other members of the fourth group and those of the third group depends on the solubility of uranium hydroxide and sulphide in an excess of a strong solution of an alkali carbonate. The hydroxides and sulphides of the other members of these two groups are, with the exception of iron and nickel, insoluble in alkali carbonate solutions. The hydroxides of these two metals are only slightly soluble in strong alkali carbonate solutions ; in cold dilute solutions they are almost insoluble.

The element which gives the most trouble in effecting a separation from uranium is iron. A great number of methods have been proposed, of which the best known are Pisani's ammonium carbonate¹ and Patera's sodium carbonate² methods, neither of which are very satisfactory. Rose used ammonium carbonate followed by ammonium sulphide,³ thus precipitating the iron. This latter method is far from satisfactory, especially if the uranium is small in amount. Rheineck's basic acetate method⁴ has been used with success when the uranium was present in considerable quantity.

Ether Separation.—The use of ether to effect a separation of iron from uranium was suggested by A. C. Langmuir in a recent article⁵ on the analysis of nickel ores. He found that iron could be separated from copper, manganese, aluminum, cobalt, nickel, and zinc, by taking advantage of the solubility of ferric chloride in ether free from alcohol. The chlorides of the other metals are not taken up by the ether but remain in the aqueous hydrochloric acid solution. When iron is in the ferrous condition, Rothe⁶ found that it was not taken into solution by the ether, but remained with the other metals in the aqueous solution. So it is necessary to oxidize the iron before attempting to make the separation.

EXPERIMENTAL.

The separation of iron from uranium by means of ether was tried, and, as the result, a clean and rather rapid separation has been worked out.⁷ This separation depends on the complete extraction of ferric chloride (in an aqueous hydrochloric acid solu-

¹ *Compt. rend.*, 52, 106.

² *Ztschr. anal. Chem.*, 5, 228 (1866).

³ *Ibid.*, 1, 410 (1862).

⁴ *Chem. News*, 24, 233 (1871).

⁵ *This Journal*, 22, 102 (1900).

⁶ *Chem. News*, 66, 182.

tion) by ether which is free from alcohol, and the retention of uranyl chloride in the aqueous hydrochloric acid solution.

Before undertaking the separation of iron from uranium by means of ether, two solutions containing uranium alone were treated three times with ether, as described in the following experiments, in order to test the solubility of uranyl chloride in ether. These experiments showed uranyl chloride to be entirely insoluble in ethyl ether which is free from alcohol.

The experiments which follow were made with solutions containing both uranium and iron. Measured amounts of a standard uranium nitrate solution and of a standard ferric chloride solution were placed in a small beaker and the solution twice evaporated to dryness with 10 cc. hydrochloric acid (sp. gr. 1.20). The dry mass was taken up with about 10 cc. dilute hydrochloric acid (sp. gr. 1.10) and heated till all salts were dissolved, but not long enough to lose any of the acid by volatilization. After the solution had cooled, it was poured into a 250 cc. separatory funnel and the beaker rinsed out with dilute hydrochloric acid (sp. gr. 1.10). The rinsings were added to the separatory funnel till the volume of the solution had reached 50 cc. Fifty cc. of ether, free from alcohol and previously shaken up with hydrochloric acid (sp. gr. 1.10), were added and agitated for about ten minutes, occasionally relieving the pressure in the funnel. After thoroughly shaking together, the two solutions were allowed to separate and the lower aqueous hydrochloric acid solution of uranyl chloride, containing some iron, was drawn off catching it in another separatory funnel. The ether solution of ferric chloride was washed twice with 10 cc. dilute hydrochloric acid (sp. gr. 1.10) and the washings, after allowing to separate, were run into the funnel containing the uranium.

On determining the amount of iron extracted from the hydrochloric acid solution by the ether, it was found that all the iron was not separated from the uranium by one extraction, about 10.5 per cent. of the amount taken remaining in the aqueous solution with the uranium.

On finding that all of the iron was not separated from the uranium by one "ether extraction," two extractions were made on a solution containing 0.1155 gram uranium and 0.0901 gram of iron. The first extraction was made in the same manner as outlined above, and the second as follows: The solution in the lower

separatory funnel was again shaken for about seven minutes with 50 cc. ether. After thoroughly shaking together, the two solutions were allowed to separate, and the lower aqueous hydrochloric acid layer run into a second funnel. The ether solution was twice washed with 10 cc. hydrochloric acid (sp. gr. 1.10), and the washings caught in the second funnel. The ether solution was run into a beaker which contained the ether from the first extraction. After distilling off the ether, the iron was determined by titration with 0.01 normal potassium permanganate solution. About 3.5 per cent. of the iron taken remained in the aqueous solution with the uranium.

The next five separations of iron from uranium were made by using hydrochloric acid of about 1.10 specific gravity (1 part acid (sp. gr. 1.20) and 1 part distilled water). In all cases three "ether extractions" were made, whereby practically complete separations of iron from uranium were obtained. The solutions contained from 0.0901 to 0.1802 gram iron and from 0.0962 to 0.2310 gram uranium. The amount of metal in their respective solutions was determined volumetrically, and did not vary more than 0.3 per cent. of the theoretical amounts taken.

The next five experiments were made by varying the strength of the hydrochloric acid used. The procedure was the same as above, making three extractions with ether. For the first three solutions, hydrochloric acid of about 1.133 specific gravity (2 parts acid (sp. gr. 1.20) and 1 part distilled water) was used; and for the last two solutions hydrochloric acid of about 1.066 specific gravity (1 part acid (sp. gr. 1.20), and 2 parts distilled water). The separation in both cases, of iron from uranium, was incomplete. When hydrochloric acid of 1.133 specific gravity was used, the amount of iron remaining with the uranium, after three "ether extractions," was about 6 per cent. of the amount taken. With hydrochloric acid of 1.066 specific gravity, the amount of iron which remained with the uranium after three "ether extractions," was about 25 per cent. of the amount taken.

The most complete separations of iron from uranium by means of ether are evidently obtained by using hydrochloric acid of 1.10 specific gravity. This is the same strength as was found by Speller¹ to be the best for the separation of iron from copper, manganese, aluminum, chromium, cobalt, and nickel.

¹ *Chem. News*, 83, 124 (1901).

When rather concentrated hydrochloric acid (sp. gr. 1.133) was used for the solution of the chlorides of iron and uranium, it was noticed that on diluting the aqueous solution, after agitating with ether, quite an amount of ether separated. This seems to explain the reason why iron is not readily separated from uranium by means of ether when strong hydrochloric acid is used to bring their chlorides into solution, the iron being retained by the large quantity of ether which remains with the acid solution.

The results obtained are shown in the following table:

SEPARATION OF IRON FROM URANIUM BY EXTRACTION WITH ETHER.

Experiment No.	Specific gravity of HCl used.	Volume of solution at first extraction. cc.	Number of ether extractions made.	Ether used for			Theoretical am't of uranium taken.	Amount of uranium determined in aqueous HCl solution.	Theoretical am't of iron taken.	Amount of iron determined in ether real extract.
				First extraction. cc.	Second extraction. cc.	Third extraction. cc.				
1	1.10	40	3	50	40	40	0.09625	0.09588
2	1.133	40	3	50	40	40	0.09625	0.09643
3	1.10	50	1	50	0.11550	0.13171	0.09010	0.08415
4	1.10	50	1	50	0.11550	0.14700	0.09010	0.07700
5	1.10	50	2	50	50	..	0.11550	0.12466	0.09010	0.08690
6	1.10	40	3	50	50	50	0.09625	0.09643	0.09010	0.08993
7	1.10	25	3	75	50	35	0.11550	0.11525	0.09010	0.09020
8	1.10	25	3	75	50	35	0.09625	0.09643	0.18021	0.18029
9	1.10	25	3	75	50	35	0.19250	0.19228	0.09010	0.08993
10	1.10	25	3	75	50	35	0.23099	0.23069	0.09010	0.09037
11	1.133	40	3	50	50	50	0.09625	0.10584	0.09010	0.08663
12	1.133	25	3	75	50	35	0.11550	0.12068	0.09010	0.08580
13	1.133	25	3	75	50	35	0.19250	0.20815	0.09010	0.08250
14	1.066	25	3	75	50	35	0.09625	0.20933	0.18022	0.12705
15	1.066	25	3	75	50	35	0.23099	0.27224	0.09010	0.07150

SEPARATION OF URANIUM FROM COBALT, NICKEL, AND ZINC.

Wolcott Gibbs separated uranium from cobalt, nickel, and zinc by means of hydrogen sulphide. He states that this method is much simpler than those ordinarily used, and also gave excellent results.¹ To the neutral or nearly neutral solution of the chlorides of uranium, cobalt, nickel, and zinc, add sodium acetate in excess and a few drops of acetic acid. The solution is boiled, and a rapid current of hydrogen sulphide passed through the boiling solution for half an hour. Every trace of the cobalt, nickel, and zinc is precipitated as sulphides while the whole of the uranium, and

¹ Silliman's *Am. J. Sci. and Art.*, [2], 39, 62 (1865).

any manganese, if present, remains in the boiling solution. The precipitate is thrown on a ribbed filter and quickly washed with cold hydrogen sulphide water. The precipitate is easily washed, and though the sulphides of cobalt and nickel formed in this manner are more easily oxidized than when precipitated by sodium sulphide from a boiling solution, they will be found to present no difficulty as regards oxidation upon the filter. If manganese is in the filtrate it may be determined by boiling with hydrochloric acid and precipitating it in the usual manner with sodium carbonate. The uranium in the filtrate is determined by the ordinary method.

Rose separated uranium from cobalt, nickel, and zinc by means of barium carbonate.¹ The precipitation of the uranium is complete from uranic solutions which contain a small amount of free acid, either hydrochloric or nitric acid. Barium carbonate, which is diffused in water, is added in excess and the solution allowed to stand twenty-four hours. The presence of ammonium chloride is necessary in order to keep the cobalt, nickel, and zinc in solution. The uranium is separated from the excess of barium carbonate by dissolving the precipitate in hydrochloric acid, and adding dilute sulphuric acid. The uranium in the filtrate is precipitated with ammonia, and weighed as oxide. C. Rammelsberg² employed this method to separate uranium from cobalt and nickel and obtained excellent results; but when manganese and zinc are present it cannot be advantageously employed.

SEPARATION OF URANIUM FROM THE ALKALI AND THE ALKALINE EARTH METALS.

If a solution containing uranium, alkalies, and alkaline earths is precipitated with ammonia, a portion of the alkalies and alkaline earths is carried down by the ammonium uranate,³ thus preventing a complete separation.

Hillebrand⁴ found that it is possible to completely separate uranium from the alkalies and alkaline earths by several precipitations with ammonia. In order to verify this statement, solutions containing a measured amount of standard uranium nitrate solution and sodium and potassium salts were precipitated by

¹ Rose's "Chimie Analytique—Analyse Quantitative," p. 248, (1862.)

² *Chem. Centrbl.* (1884), p. 806.

³ Fresenius' "Quantitative Chemical Analysis," 6th edition, p. 533.

⁴ *Am. J. Sci.*, 10, 136 (1900).

means of a slight excess of ammonia, and the solutions brought to boiling. The precipitates were washed with a warm 2 per cent. solution of ammonium chloride, after which they were dissolved from the filters with warm hydrochloric acid (sp. gr. 1.10) and caught in beakers. The precipitation of the uranium by ammonia, in the presence of ammonium chloride and from hot solutions, was repeated twice, and it was found that after three precipitations the ammonium uranate was free from alkalies.

Magnesium may be separated from uranium by means of ammonium sulphide in the presence of ammonium chloride¹ and also by ammonia in the presence of an excess of ammonium chloride. The latter method is the one ordinarily used.² To the solution containing uranium and magnesium, add ammonium chloride and boil. When the solution becomes clear, add a slight excess of ammonia to the hot solution and continue boiling for a few minutes. Filter while hot and wash the precipitate with hot water containing ammonium chloride. Dry, ignite, and weigh the uranium as oxide.

The separation of uranium from barium, strontium, and calcium is usually done by means of sulphuric acid in the presence of alcohol.³ The metals should be in solution as chlorides, having present the smallest possible amount of free hydrochloric acid. To the moderately dilute solution, add sulphuric acid, then alcohol, which precipitates the barium, strontium, and calcium, in the form of sulphates. The uranium in the filtrate is precipitated with ammonia and weighed as oxide.

The separation of uranium from barium, strontium, and calcium, may be brought about by precipitating the uranium with freshly prepared ammonium sulphide (free from carbon dioxide).⁴

In 1885, G. Alibigoff studied the action of mercuric oxide on uranium solutions and found a means of separating uranium from the alkalies and alkaline earths.⁵ He showed that neither ammonium sulphide, nor ammonium carbonate followed by ammonium oxalate, can be successfully employed for separating uranium from calcium. The latter method is, however, preferable to the first. He states that a com-

¹ *Ztschr. anal. Chem.*, 4, 384 (1865).

² Fremy's "Encyclopédie Chimique," p. 86, (1884).

³ *Ibid.*, p. 86, (1884).

⁴ Fresenius' "Quantitative Chemical Analysis," p. 534.

⁵ *Ann. Chem. (Liebig)*, 233, 147 (1886).

plete separation of uranium from calcium, strontium, magnesium and the alkalies can be effected by the use of mercuric oxide; it does not, however, afford a separation of uranium from barium. The precipitation is made by adding a slight excess of freshly prepared mercuric oxide (in the form of an emulsion) to the boiling solution which contains ammonium chloride or nitrate. The boiling is continued for a few minutes longer and then rapidly cooled by placing the vessel into cold water. Wash the precipitate by decantation with a cold dilute solution of ammonium chloride. It is placed along with the filter in a platinum crucible, cautiously heated at first, after which the temperature is gradually raised and finally ignited over a blast-lamp. The residue consists of pure U_3O_8 . The separation of uranium from the alkali metals by this method does not give any undue trouble, but when calcium and strontium are present they are rather hard to rid from the uranium precipitate. This difficulty is overcome by boiling several times, during washing by decantation, with a solution of ammonium chloride and each time rapidly cooling the solution before pouring off the supernatant liquid. The calcium and strontium in the filtrate are determined by the ordinary methods after the removal of the mercury by hydrogen sulphide.

SEPARATION OF URANIUM FROM THE ALKALI AND ALKALINE EARTH METALS BY ELECTROLYSIS OF ACETATE SOLUTION.

Uranium is a very difficult metal to separate from the alkalies and alkaline earths by gravimetric methods; but by electrolyzing an acetate solution of these elements a perfect separation can be effected¹. It can be readily separated from sodium, potassium, rubidium, cesium, magnesium, calcium, strontium, and barium. This method was used by E. F. Smith for separating uranium from the alkalies, the alkaline earths, and the rare earths in the analysis of certain rare minerals.

A very peculiar property of uranium is that it is not deposited as metal on the cathode, but as the hydrated protosesquioxide. Molybdenum is the only other metal known which, like uranium, is deposited as oxide on the cathode.

EXPERIMENTAL.

This research was made in order to fully confirm the reliability of the electrolytic method for the estimation of uranium and its

¹ *Am. Chem. J.*, 1, 329 (1879); this Journal, 20, 279 (1898).

separation from the alkalies, and also to find the conditions which are best suited for rather dilute solutions.

The cathodes for the first six experiments, when a current of $N.D_{140} = 0.6$ to 0.7 ampere was employed, were two platinum dishes of about 250 cc. capacity. For experiments Nos. 7 to 10, the cathode was a platinum dish of about 150 cc. capacity.

The anodes were made of heavy platinum wire. One was made of 30 cm. of No. 12 gauge platinum wire wound into a flat spiral of 4 cm. diameter. The other anode was made of 37 cm. of No. 14 gauge platinum wire wound into a flat spiral of 4 cm. diameter. The results obtained by the use of either anode were the same.

Storage cells were the source of current.

For the electrolysis, a measured amount of standard uranium nitrate solution was run into a cleaned and weighed platinum dish. A known amount of sodium acetate and of acetic acid was added, and the solution diluted to a definite volume. After heating to about 60° C., the current was started and the electrolyzation continued till the solution was clear and colorless, and no uranium was indicated when about 2 cc. of the electrolyte was removed and tested with potassium ferrocyanide in the presence of hydrochloric acid. As soon as all the uranium was precipitated, the current was interrupted and the electrolyte was emptied into a beaker. The black deposit was several times washed with warm distilled water. The electrolyte and washings were then poured through a fluted filter, so as to prevent the loss of any particles of the deposit which are apt to be removed during washing. The filter was washed with warm water, dried over a Bunsen flame, ignited, and added to the dish. The dish was ignited at "redness" for about fifteen minutes, after which it was allowed to cool in a desiccator. The dish was weighed and the final weight taken when it had remained on the balance pan for about five minutes, thus allowing its weight to become constant.

The deposit consisted principally of black hydrated protosesquioxide of uranium ($U_2O_4 \cdot 3H_2O$), which on ignition changed to U_3O_8 .

At the beginning of the electrolysis the deposit formed as yellow uranic hydroxide, but as the deposition continued it changed to the black hydrated protosesquioxide.

The results obtained¹ are :

Experiment No.	Drops.	Grams of sodium acetate.	Amount of glacial acetic acid. cc.	Current.			Time in hours.	Theoretical am't of U_3O_8 taken.	Weight of deposited U_3O_8 .
				Dilution.	Current, N.D. ₁₄₀ = ampere.	Volts.			
1	2	0.7	200	0.55	5	68-70	8	0.1098	0.1095
2	2	12	200	0.60	5	70	7	0.1098	0.1097
3	2	0.5	200	0.60-0.65	8-6	68-75	5	0.1098	0.1100
4	2	0.5	200	0.65	8-7.3	65-67	5½	0.1318	0.1319
5	2	0.5	200	0.65	7.5-6	68-70	5	0.1318	0.1318
6	2	0.5	200	0.60-0.65	8-5.5	69-71	5½	0.1318	0.1320

These results were obtained by electrolyzing a solution of 200 cc. volume with a current of N.D.₁₄₀ = 0.55 to 0.65 ampere.

The results obtained, when a solution of 125 cc. was electrolyzed with a current of N.D.₁₀₀ = 0.70 to 1.50 ampere, are as follows :

Experiment No.	Grams of sodium acetate.	Amount of 50 per cent. acetic acid. cc.	Dilution.	Current, N.D. ₁₀₀ = ampere.	Temperature.	Time in hours.	Theoretical am't of U_3O_8 taken.	Weight of deposited U_3O_8 .
7	1.0	2	125	0.70-0.85	80-85 °C.	6	0.1361	0.1363
8	2.0	2	125	0.70-0.93	70-80	6½	0.1814	0.1816
9	2.0	2	125	0.95-1.50	70-75	7½	0.2268	0.2270
10	0.3	1	125	0.90-1.30	73-80	8	0.2268	0.2260

According to the above results, the best conditions for the electrolytic precipitation of uranium from a rather dilute acetate solution are as follows: To the solution containing about 0.10 gram of U_3O_8 add from 1 to 2 grams of sodium acetate (if alkalies are present, no sodium acetate is needed) and from 1 to 2 cc. of 50 per cent. acetic acid, or if glacial acetic acid is used only half the quantity is needed. Dilute to from 125 to 200 cc., heat to about 65° C. and electrolyze with a current of N.D.₁₄₀ = 0.60 to 0.70 ampere and 6 to 8 volts. The uranium is completely precipitated in from five to seven hours.

With solutions containing about 0.15 gram of U_3O_8 more current

¹ This part of the work, including experiments 1-6, was done under the direction of Prof. E. F. Smith at the University of Pennsylvania, during April, 1900.

is necessary, and the best conditions are: Add from 1 to 2 grams of sodium acetate, and from 1 to 2 cc. of 50 per cent. acetic acid, dilute the solution to 125 cc. and electrolyze with a current of $N.D_{100}$ = from 0.70 to 1.0 ampere. The temperature of the solution should be about 65° to 70° C. After the current is started no heat need be applied outwardly as the current itself keeps the solution heated. The time required for the complete precipitation of about 0.15 gram of U_3O_8 is from six and one-half to seven and one-half hours.

When solutions containing more than 0.15 gram of U_3O_8 were electrolyzed, some difficulty was experienced in precipitating all within eight hours by a current not exceeding $N.D_{100}$ = 1 ampere. With a current greater than this the deposits were very spongy and peeled from the dish; so the amount of U_3O_8 in solution should not exceed 0.15 gram.

The electrolytic precipitation of uranium has been used a number of times for the estimation of uranium and for separating it from the alkalies and alkaline earths. The results obtained were concordant with those obtained by precipitating it gravimetrically.

The simplicity of the electrolytic method for the determination of uranium, and the short time required, are in favor of this method.

SEPARATION OF URANIUM FROM PHOSPHORIC ACID.

Review of Methods.

*Reynoso's Method.*¹—The uranium compound should be in solution as nitrate, having a small amount of free nitric acid present. Dilute to about 150 cc., add a strip of pure metallic tin, and boil. The phosphoric acid unites directly with the tin, to form oxyphosphate of tin, which is insoluble. The precipitate is filtered off and thoroughly washed. The filtrate is made alkaline with ammonia, and the precipitate which forms is treated with acetic acid. If it does not entirely dissolve, nitric acid is added and the precipitation by pure metallic tin repeated.² Heat the solution to boiling, filter off the oxyphosphate of tin, and wash with warm water. The precipitate rarely contains any uranium. The tin in the filtrate is removed by

¹ *Ann. Chem. (Liebig)*, 81, 368 (1852).

² Fremy's "Encyclopédie Chimique," p. 86, (1884).

means of hydrogen sulphide. The filtrate from the tin sulphide is boiled till all hydrogen sulphide is expelled, after which the uranium is determined by any of the ordinary methods.

W. Hintz¹ had occasion to investigate this method and stated that a complete separation of phosphoric acid from uranium is effected by means of metallic tin.

*Knopp and Arendt Method.*²—The separation of uranium from phosphoric acid may be effected by fusing the ignited mass of uranium and phosphoric acid with a mixture of potassium cyanide and potassium carbonate, and treating the fused mass with warm water to dissolve out the phosphoric acid as soluble alkaline phosphate. The uranium is left as protoxide, which is reignited and weighed, or else dissolved in acid and precipitated by ammonia. The phosphoric acid in the filtrate is precipitated with magnesia mixture and weighed as magnesium pyrophosphate. Hintz³ used sodium carbonate in place of potassium carbonate, and obtained very satisfactory results.

*E. Reichardt's Method.*⁴ is based on the direct precipitation of phosphoric acid, from an acetate solution as uranyl-ammonium phosphate, provided the uranium is in excess. The precipitate is filtered off, washed, dissolved in a solution of sodium carbonate, and the solution added to a solution of magnesia mixture, which precipitates the phosphoric acid as magnesium ammonium phosphate. If iron is present it is first precipitated from a nitric acid solution by adding an excess of sodium carbonate and boiling.⁵ The phosphoric acid in the filtrate is precipitated as magnesium ammonium phosphate, and the uranium determined by the ordinary method, after expelling all the carbon dioxide.

*Fresenius and Hintz Method.*⁶—This method provides a means of separating arsenic and phosphoric acid from copper, uranium, and iron. Have the solution feebly acid with hydrochloric acid, add an excess of potassium ferrocyanide, then saturate with sodium chloride. The ferrocyanides of copper, uranium, and iron are washed by decantation, and subsequently decomposed by a warm solution of caustic potash, changing them to hydroxides.

¹ Ann. Chem. (Liebig), 181, 216 (1869).

² Chem. Centrbl., 773, (1856).

³ Ann. Chem. (Liebig), 181, 216 (1869).

⁴ Ztschr. anal. Chem., 8, 116 (1869); Bull. Soc. Chim., 20, 347 (1873).

⁵ Ztschr. anal. Chem., 8, 116 (1869).

⁶ Ibid., 34, 437; Chem. News, 72, 206 (1895).

Filter and wash with a dilute solution of ammonium chloride till no ferrocyanide is recognized in the washings. The mixed hydroxides are treated with dilute hydrochloric acid. If any residue remains it is decomposed by a warm solution of caustic potash, going through with the same treatment as before. The solution by hydrochloric acid is free from arsenic and phosphoric acid. The copper, iron, and uranium are separated by ordinary methods.

*Friedel and Cumenge*¹ separated phosphoric acid from uranium by dissolving the substance in nitric acid, and precipitating the phosphoric acid with ammonium molybdate.

This method was used² for estimating the amount of phosphoric acid in precipitates of uranous phosphate, which were formed by electrolysis. The sample was dissolved in 30 cc. nitric acid (sp. gr. 1.42) and 3 cc. hydrochloric acid (sp. gr. 1.20). When iron was present, the sample was dissolved in a mixture of 20 cc. hydrochloric acid (sp. gr. 1.20) and 10 cc. nitric acid (sp. gr. 1.42). The solution was diluted to about 100 cc., and nearly neutralized with ammonia. A few drops of nitric acid were added to clear the solution, making it slightly acid, then to the hot solution (not above 65° C.) 50 cc. of molybdate solution³ for every decigram of phosphorus pentoxide present. After digesting at 65° C. for an hour and a half, the yellow precipitate was filtered, and washed with cold water. The filtrate was tested for phosphoric acid by adding more molybdate solution and reheating at 65° C. The yellow precipitate of ammonium phosphomolybdate was dissolved from the filter with ammonia and hot water, and washed into a beaker to a bulk not exceeding 100 cc. It was nearly neutralized with hydrochloric acid, cooled, and magnesia mixture added, drop by drop from a burette, stirring all the while. After about twenty minutes, 30 cc. ammonia (sp. gr. 0.96) were added and the solution allowed to stand in the cold for three hours. The precipitate of magnesium ammonium phosphate was filtered and washed with dilute ammonia (2.5 cc. ammonia and 100 cc. water) till free from chlorides. The precipitate was dried, ignited, and weighed as magnesium pyrophosphate.

The uranium in the filtrate, from the ammonium phospho-

¹ *Am. J. Sci.*, 10, 135 (1900).

² At the University of Pennsylvania in 1900.

³ Prepared according to the formulas given in the "Official Methods of the U. S. Agricultural Chemists."

molybdate, was determined by three precipitations with ammonia, and weighed as U_3O_8 .

PART II.—THE DETERMINATION OF URANIUM.

DETERMINATION OF URANIUM AS OXIDE.

The precipitant which Pélidot used in 1840 for the estimation of uranium was ammonia, the principal reagent used for that purpose at the present time. The yellow precipitate which forms when ammonia is added to a uranyl solution is hydrated ammonium uranate¹ ($(\text{NH}_4)_2\text{U}_2\text{O}_7 \cdot x\text{H}_2\text{O}$, or $(\text{NH}_4)_2\text{O} \cdot 2\text{UO}_3 \cdot x\text{H}_2\text{O}$), which is soluble in alkali carbonate solutions, and slightly soluble in pure water; but in water containing ammonia, ammonium nitrate, or ammonium chloride it is insoluble.² The presence of tartaric acid, oxalic acid, or non-volatile organic substances prevents the precipitation of ammonium uranate.³

If the solution contains any alkalies or alkaline earths, a portion of these will be precipitated along with the uranium.⁴

*Berthier's Method.*⁵—The reagent next in importance to ammonia, for the estimation of uranium, is ammonium sulphide, which was first used (in 1840) by Berthier. A complete precipitation of uranium by ammonium sulphide is obtained, provided the solution is previously nearly neutralized by ammonia, and no carbonates are present. The precipitate which forms is usually black in color, sometimes changing to reddish brown.⁶ When a large excess of the precipitant is added and it is allowed to stand, the liquid sometimes assumes a brown color.⁷ This color, says Zimmerman,⁸ is due to the solubility of uranyl sulphide in ammonium carbonate contained in the ammonium sulphide. When the ammonium sulphide contains a considerable amount of thiosulphate the red sulphide described by Remele⁹ is formed; but when thiosulphate is absent only the dark precipitate results. Thiosulphate in the reagent is due to the oxidation of ammonium sulphide by atmospheric oxygen.

In 1865, A. Remele studied the method for the estimation of

¹ *Chemiker Kalender*, p. 270, (1899).

² Comey's "Dictionary of Chemical Solubilities."

³ Fresenius' "Qualitative Chemical Analysis," 219.

⁴ *Ibid.*, 6th edition, p. 533.

⁵ *Ann. Chem. (Liebig)*, 46, 184.

⁶ *Pogg. Ann.*, 116, 352.

⁷ *Ibid.*, 124, 120.

⁸ *Ann. Chem. (Liebig)*, 204, 224 (1880).

⁹ *Pogg. Ann.*, 116, 352.

uranium by the use of ammonium sulphide and found the best results were obtained by the following procedure:¹ The ammonium sulphide should be fresh and kept well corked, as it absorbs carbon dioxide when exposed to the atmosphere. To the nearly neutral ammoniacal solution, add an excess of yellow ammonium sulphide and keep the solution near boiling for an hour, in order to convert the $(\text{UO}_2)\text{S}$, which is first formed, into a mixture of UO_2 and sulphur. This precipitate is rapidly dissolved by alkali carbonates and by tartaric acid. It is slightly soluble in pure water, is soluble in dilute, but insoluble in absolute, alcohol. It is readily soluble in acids, even acetic acid.² The presence of ammonium chloride or ammonium nitrate assists the precipitation of $(\text{UO}_2)\text{S}$, as it is less soluble in these solutions. The precipitate, containing all the uranium, is filtered off and washed with cold or hot water containing a small amount of ammonium sulphide and ammonium chloride or nitrate. Wash first by decantation and finally on the filter. The precipitate during washing passes to yellow uranic hydroxide. It is dried, then roasted to remove all the sulphur and finally converted into U_3O_8 by ignition in the air, or into UO_2 by ignition in a current of hydrogen and allowing to cool in same.

A complete separation of uranium from the alkalies and alkaline earths is obtained by means of ammonium sulphide.³

C. Winkler made a comparison of this method with Péligot's ammonium method⁴ and states that the precipitation of uranium by pure ammonium sulphide is trustworthy.⁵

EXPERIMENTAL.

Precipitation of Uranium by Ammonia.—For each determination a measured amount of standard uranium nitrate solution was run into a beaker and enough distilled water added to bring the volume to from 150 to 200 cc. The solutions were brought to boiling and a few drops of nitric acid added, and the uranium precipitated by adding an excess of ammonia to the hot solution. The precipitates which formed were a bright lemon-yellow color and settled rapidly. The precipitates were allowed to settle, and washed several times by decantation and twice on the filter with

¹ *Ztschr. anal. Chem.*, 4, 379.

² Comey's "Dictionary of Chemical Solubilities," 1896.

³ *Ztschr. anal. Chem.*, 1, 411.

⁴ Fresenius' "Quantitative Chemical Analysis," p. 281.

⁵ *Chem. News*, 43, 153 (1881).

warm dilute ammonium chloride solution (2 grams salt to 100 cc. water), after which they were dried in a hot oven, and ignited and weighed as oxides.

The following table gives the conditions observed :

THE THEORETICAL AMOUNT OF URANIUM TAKEN WAS 0.1925 GRAM.

No.	Experiment No.	Approximate dilution. cc.	Salts present.	Crucible in which ignited.	Weighed as:	Weight of U_3O_8 .	Uranium equivalent of U_3O_8 .	Ignited in hydrogen for:	Weight of UO_2 .	Uranium equivalent of UO_2 .
1	200	NH_4Cl	Platinum	U_3O_8	0.2242	0.19130
2	200	NH_4Cl	Platinum	U_3O_8	0.2268	0.19252
3	150	NH_4Cl	Platinum	U_3O_8	0.2269	0.19260
4	150	NH_4Cl	Platinum	U_3O_8	0.2266	0.19235
5	175	NH_4Cl	Platinum	U_3O_8	0.2268	0.19252	2	0.2191	0.19329	0.19329
6	175	{ NH_4Cl CHCl ₃	Platinum	{ U_3O_8 UO_2	0.2267	0.19243	½	0.2179	0.19223	0.19223
7	175	{ NH_4Cl CHCl ₃	Porcelain	U_3O_8	0.2269	0.19260	2½	0.2207	0.19479	0.19479
8	150	NH_4Cl	Platinum	U_3O_8	0.2268	0.19252	1	0.2211	0.19505	0.19505
9	150	NH_4Cl	Platinum	U_3O_8	0.2270	0.19268	¼	0.2221	0.19593	0.19593
10	150	{ NH_4Cl Alcohol	Porcelain	U_3O_8	0.2280	0.19353
11	175	{ NH_4Cl Alcohol	Porcelain	U_3O_8	0.2270	0.19268
12	175	NH_4Cl	Platinum	UO_2	½	0.2180	0.19232	0.19232
13	150	NH_4Cl	Porcelain	1	0.2240	0.19761	0.19761

U_3O_8 multiplied by 0.84884 gives the uranium equivalent; UO_2 multiplied by 0.88218 gives the same. These are the factors obtained by taking the atomic weight of uranium as 239.6 and that of oxygen as 16.¹

For all the above precipitations the solutions, of from 150 to 200 cc. volume, were made decidedly acid with from 0.5 to 1 cc. nitric acid (sp. gr. 1.42), brought to boiling and ammonia added in excess. Some of the solutions were boiled for about fifteen minutes after the precipitation by ammonia, while others were filtered directly without boiling. The boiling caused the lemon-yellow colored voluminous amorphous precipitate to change to a more crystalline form, less voluminous and of a slightly darker color. The precipitates which were boiled were much easier to filter and wash, and were less liable to pass through, which usually happened when boiling was omitted.

¹ This Journal, 23, 94 (1901).

The presence of chloroform or alcohol (as recommended by some chemists) did not assist the precipitation, but the presence of ammonium chloride or ammonium nitrate was essential. Five to ten grams were added previous to the addition of ammonia.

Some of the precipitates were ignited separate from the paper, and others without separating from the paper. The results obtained, whether the precipitates were ignited separately or not, were identical, showing that it is unnecessary to ignite the precipitate and the filter-paper separately, as is recommended by the German chemists.

When the uranium was weighed as U_3O_8 , the precipitates together with the filter-paper were placed in a crucible and slowly ignited till the paper had completely burned; then the ignition was continued for about fifteen minutes in a blast-flame, and allowed to cool slowly in a gradually decreasing Bunsen flame. During ignition the crucibles were placed in a slanting position in order to allow of free circulation of air in the crucible, thus obtaining complete oxidation. The results were the same whether porcelain or platinum crucibles were used.

In all directions given in text-books and journals for weighing uranium as oxide, it is recommended that the dry precipitate of ammonium uranate be strongly ignited over a blast-lamp to U_3O_8 , and allowed to slowly cool in a gradually decreasing flame and finally in a desiccator. It is then weighed, and as a means of ascertaining its purity for the purpose of control, it is reignited in a current of pure hydrogen and reduced to its lower oxide, UO_2 . This was tried, but only in one case was it possible to completely reduce U_3O_8 to UO_2 , even when the ignition in hydrogen was continued for two hours. This time (experiment No. 6) the reduction was brought about by using a platinum crucible and igniting strongly in a current of pure hydrogen over the hottest blast-lamp that could be obtained. When a porcelain crucible was used in which the ignition was made, the reduction did not proceed so far as when a platinum crucible was used. The reason for this is the fact stated by Roberts-Austen¹ as follows: "Saint Claire Deville and Troost discovered that hydrogen and hydrocarbons pass through platinum at a red heat." The further reduction of U_3O_8 , when a platinum crucible is used, would seem to indicate that hydrocarbons of the flame play as important a

¹ Roberts-Austen's "Introduction to Metallurgy," p. 54, (1898).

part in the reduction as the hydrogen. It was impossible to obtain a single complete reduction of the precipitate to UO_2 , when a porcelain crucible was used, even when the precipitate was not previously ignited. When a platinum crucible was used, and the precipitate not previously ignited in the air, the complete reduction to UO_2 , occurred within half an hour by igniting it in a current of pure hydrogen over a blast-lamp, and allowing it to cool in an atmosphere of hydrogen over a gradually decreasing flame. The U_2O_8 is a velvety black colored mass, and the UO_2 , a dull brown colored mass.

For the above reductions ordinary porcelain and platinum Rose crucibles were used. The hydrogen was purified by Schobig's method,¹ by first passing it through a strong solution of potassium permanganate to remove the hydrides of arsenic, antimony, phosphorus, and carbon; then through a strong solution of caustic soda to remove hydrogen sulphide; and finally through sulphuric acid (sp. gr. 1.84) to remove moisture.

DETERMINATION OF URANIUM AS PHOSPHATE.

Review of Method.

The precipitation of uranium by an alkali phosphate has rarely been employed as a means of estimating uranium, because the precipitate which forms is gelatinous and difficult to wash free from alkali. This trouble has been overcome by adapting the method to volumetric means, which is the reverse of the volumetric estimation of phosphoric acid by a standard uranium solution. The uranium in solution as acetate is titrated by means of a standard solution of sodium-hydrogen-ammonium phosphate ($\text{NaHNH}_4\text{PO}_4$), which is added till a drop of the precipitated solution brought in contact with a drop of freshly prepared solution of potassium ferrocyanide does not give a brown coloration.²

The quantitative estimation of uranium by means of an alkali phosphate was first suggested by Leconte³ and later worked out by Pisani;⁴ but owing to the difficulty of filtering and washing the greenish yellow, slimy precipitate of UO_2HPO_4 , this method has not come into use.

¹ *J. prakt. Chem.*, (2), 14, 289-299.

² Mohr's "Lehrbuch der Chemisch-analytischen Titrirmethode," p. 521. Dammer's "Handbuch der anorg. Chemie," 3, 686 (1893).

³ Liebig and Kopp: *Jahresbericht*, p. 642, (1853).

⁴ *Chem. News*, 3, 211 (1862).

EXPERIMENTAL.

Were it not for the difficulty of washing the uranium phosphate, which is formed by disodium hydrogen phosphate, this method would afford a decided advantage over precipitating it with ammonia and weighing it as oxide (U_3O_8) because any error would be greatly diminished by weighing as $(UO_2)_2P_2O_7$. U_3O_8 multiplied by 0.84884 gives the uranium equivalent, while $(UO_2)_2P_2O_7$ multiplied by 0.66815 gives the same; so by weighing the uranium as pyrophosphate the error or loss is decreased.

This method was studied, and the best conditions for weighing uranium as uranyl pyrophosphate were worked out, the results of which are tabulated below.

PRECIPITATION OF URANIUM BY DISODIUM HYDROGEN PHOSPHATE.

Experiment No.	Approximate dilution, cc.	Salts added.	Temperature of solution after precipitation.	Crucible in which ignited.	Time of ignition, Minutes.	Weight of $(UO_2)_2P_2O_7$	Uranium equivalent.	Theoretical amount of uranium taken.
1 150	{ $\begin{matrix} NH_4NO_3 \\ NN_4C_2H_5O_2 \end{matrix}$	{ Cold, then heated to b.p.	Platinum	15	0.2875	0.1921	0.1925	
2 150	{ $\begin{matrix} NH_4Cl \\ NH_4C_2H_5O_2 \end{matrix}$	"	"	10	0.2884	0.1927	0.1925	
3 150	{ $\begin{matrix} NH_4NO_3 \\ NH_4C_2H_5O_2 \end{matrix}$	"	Porcelain	10	0.2878	0.1923	0.1925	
4 150	{ $\begin{matrix} NH_4NO_3 \\ NH_4C_2H_5O_2 \end{matrix}$	{ b.p. for 1 hour after precipit.	Platinum	10	0.2851	0.1905	0.1925	
5 150	{ Chloroform	"	"	10	0.2848	0.1903	0.1925	
6 150	{ $\begin{matrix} NH_4NO_3 \\ NH_4C_2H_5O_2 \end{matrix}$	"	Porcelain	15	0.2875	0.1921	0.1925	
7 150	{ Chloroform	"	"	20	0.2870	0.1918	0.1925	

These determinations were made by measuring 50 cc. of standard uranium nitrate solution into a beaker, diluting to 150 cc. and adding nitric acid (sp. gr. 1.42), varying the amount from 0.5 cc. to 1.5 cc. The solutions were brought to boiling and ammonia (sp. gr. 0.90) added to neutral reaction and a measured amount in excess—from 1 cc. to 10 cc. The yellow precipitate of ammonium uranate was dissolved by adding 50 per cent. acetic acid till the precipitate disappeared, and then an excess varying from 1 cc. to 5 cc. To the solution—which contained besides uranium acetate, an excess of acetic acid, ammonium nitrate, and

ammonium acetate—an excess of a saturated solution of disodium hydrogen phosphate was added. The precipitate which formed was greenish white in color and voluminous. The solution was brought to boiling, then allowed to cool, and filtered. In experiments Nos. 4 to 7 the solutions were kept for one hour on water-baths at the temperature of boiling water, after which they were allowed to cool, then filtered. This treatment assisted the settling of the precipitate, but did not change its gelatinous character.

The washing of the precipitates was done by four decantations and twice on the filter with a hot dilute solution of ammonium chloride (2.5 grams of salt to 100 cc. of water). The washing was not so easy as the ammonium uranate precipitates, even when as much as 5 grams of ammonium chloride were added to the solution previous to its precipitation. Neither the addition of chloroform nor of ammonium chloride had any effect on the appearance of the precipitate, as there were already sufficient ammonium salts present, formed by the neutralization of nitric acid by ammonia and of ammonia by acetic acid.

The precipitates, after washing, were dried at a temperature of from 100° C. to 115° C., separated from the filter-paper, which was first ignited in the crucible, then the precipitate added and the ignition continued for from ten to twenty minutes at "redness" over a Bunsen burner. The residue in most cases was green in color, due to the partial reduction of uranyl pyrophosphate. Whenever the temperature of ignition was above "redness" a reduction always occurred, especially when a platinum crucible was used. When a porcelain crucible was used the ignition could be done at "redness," but above this temperature (as over a blast-lamp) reduction always resulted.

The reduced uranyl pyrophosphate was not weighed as such, but was moistened with a few drops of nitric acid (sp. gr. 1.42), dried over a low flame, and reignited at "low redness" over a Bunsen burner. The mass after such treatment was always of a lemon-yellow color. The weight of the yellow uranyl pyrophosphate remained constant, no matter how long it was ignited at a temperature not exceeding "low redness," but above this temperature it always lost weight and assumed a green color. Whenever this occurs it may be reoxidized by treating it with nitric acid and reigniting at "low redness."

This green residue of pyrophosphate most probably has the composition $U_2O_7P_2O_7$, which is indicated by the weights of several which varied from 0.2820 to 0.2827 gram. 0.2820 multiplied by 0.6833 gives 0.1929 gram uranium, the theoretical amount of uranium being 0.1925 gram.

One of the residues which was more intensely ignited than the others, with the cover on the platinum crucible, was of a reddish brown color. Its weight was 0.2800 gram, showing that the reduction had gone further than $U_2O_7P_2O_7$.

The composition of the lemon-yellow colored uranyl pyrophosphate is $(UO_2)_2P_2O_7$.

PRECIPITATION OF URANIUM BY AMMONIUM DIHYDROGEN PHOSPHATE.

As the precipitates formed by disodium hydrogen phosphate were slimy and difficult to wash, it was suggested that possibly this difficulty could be overcome by means of an ammonium phosphate. The precipitant used was ammonium dihydrogen phosphate. The mode of procedure was the same as when disodium hydrogen phosphate was used.

To a solution containing 0.1925 gram of uranium were added from 0.1 cc. to 1.5 cc. nitric acid (sp. gr. 1.42) and sufficient water to make 150 cc. volume. The solution was brought to boiling, ammonia (sp. gr. 0.90) was added to neutral reaction and from 1 cc. to 10 cc. in excess. The ammonium uranate which formed was taken into solution by the addition of 50 per cent. acetic acid and from 1 cc. to 5 cc. in excess. The solutions, then acid with acetic acid, were brought to boiling and the uranium precipitated by an excess of a saturated solution of ammonium dihydrogen phosphate. The best precipitations, that is, those which were most crystalline and easiest to handle, were formed when about one and a half as much precipitant was added as was necessary for the precipitation. The solutions were boiled for half an hour, and the precipitate allowed to settle before filtering. The precipitates were washed three times by decantation and three times on the filter with a hot dilute solution of ammonium chloride (2 grams salt to 100 cc. water). The addition of ammonium chloride or of chloroform to the solution was found unnecessary, as enough ammonium salts were already present. The precipitates which formed were pulverulent and crystalline,

and were as readily filtered and washed as the precipitates of ammonium uranate.

The precipitates were dried, separated from the filter-paper, and the paper ignited in a porcelain crucible, after which the precipitate was added and the ignition continued at "redness" for about five minutes. The crucible was allowed to cool and the residue moistened with a few drops of nitric acid (sp. gr. 1.42). The mass was dried over a low flame, then reignited for from ten to twenty-five minutes at "low redness" over a Bunsen burner. The mass after this treatment was, in all cases, a lemon-yellow color. The crucibles were allowed to cool in a desiccator, and weighed.

The results obtained are as follows:

PRECIPITATION OF URANIUM BY AMMONIUM DIHYDROGEN PHOSPHATE.

Experiment No.	Approximate dilution. cc.	Salts added.	Temperature of solution after precipitation.	Crucible in which ignited.	Time of ignition. Minutes.	Weight of $(\text{UO}_2)_2\text{P}_2\text{O}_7$.	Uranium equivalent.	Theoretical amount of uranium taken.
8 150	{ NH_4NO_3 $\text{NH}_4\text{C}_2\text{H}_5\text{O}_2$	{ b.p., boiled for 1 hour.		Porcelain	10	0.2879	0.1924	0.1925
9 150	"	{ b.p., boiled for 10 min.	"		15	0.2880	0.1924	0.1925
10 200	"	{ b.p., boiled for $\frac{1}{4}$ hour.	"		20	0.2881	0.1925	0.1925
II 200	"	"	"		20	0.2879	0.1924	0.1925
12 150	{ NH_4Cl NH_4NO_3 $\text{NH}_4\text{C}_2\text{H}_5\text{O}_2$	"	"		25	0.2881	0.1925	0.1925
13 150	{ NH_4NO_3 $\text{NH}_4\text{C}_2\text{H}_5\text{O}_2$	"	"		25	0.2883	0.1926	0.1925
14 200	"	"	"		15	0.2879	0.1924	0.1925
15 150	{ NH_4Cl $\text{NH}_4\text{C}_2\text{H}_5\text{O}_2$	"	"		15	0.2878	0.1923	0.1925
16 150	"	"	"		15	0.2882	0.1926	0.1925

The filtrates were evaporated and tested for uranium with potassium ferrocyanide. No uranium was indicated.

In several cases when the ignition was done at a temperature above "redness," the precipitate would invariably assume a green color, especially where the residue was in contact with the crucible. Whenever this occurred, the mass was again moistened with nitric acid (sp. gr. 1.42), dried over a low flame, and reigned at "low redness." By this treatment the mass was oxidized to $(\text{UO}_2)_2\text{P}_2\text{O}_7$.

Several precipitates, after having been weighed as uranyl pyrophosphate, were reignited over a blast-lamp for about fifteen minutes. The residue, in all cases, after such treatment was entirely green, but when moistened with nitric acid (sp. gr. 1.42) and reignited at "low redness," always changed back to lemon-yellow uranyl pyrophosphate, and their weight was the same as the original weight.

Solution No. 15 was allowed to stand for six days before filtering. The appearance of the precipitate was the same as those which were filtered directly.

The weighing of uranium as uranyl ammonium phosphate ($\text{UO}_2 \cdot \text{NH}_4 \cdot \text{PO}_4$) was undertaken, but without success. The filtering through Gooch crucibles was tried, but owing to the fineness of the precipitate this could not be done. After trying to filter six solutions in this manner, the idea of weighing uranium as uranyl ammonium phosphate was abandoned as impracticable.

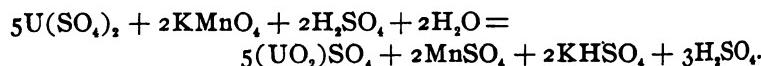
THE VOLUMETRIC ESTIMATION OF URANIUM.

Belohoubeck,¹ in 1866, estimated uranium by reducing the solution in a flask with metallic zinc and sulphuric acid. For small amounts of uranium, he states that the reduction is complete in about fifteen minutes, while for larger quantities the time required is much longer. The solutions, after reduction, were diluted and titrated by a standard potassium permanganate solution, the standard of which was made on ferrous ammonium sulphate.

Uranium differs from iron, as regards reduction, in that it is not reduced by hydrogen sulphide. When mercuric salts are present the uranium is, however, reduced by this reagent.²

The permanganate used for titrating uranium solutions is standardized by iron, two atoms of iron corresponding to one of uranium.

The reaction³ which occurs during the titration of sulphate solutions of uranium is :

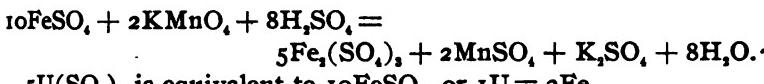


The reaction which occurs during the titration of ferrous solution is :

¹ *Ztschr. anal. Chem.*, 6, 120 (1867); Sutton's "Volumetric Analysis," p. 375. (1900).

² Dammer's "Handbuch der anorg. Chemie," Vol. III, p. 686 (1893).

³ Mohr's "Lehrbuch der chem.-analyt. Titrirmethoden," p. 267.



The reduction of uranium by zinc and sulphuric acid corresponds to the change of UO_2 to UO_2^{+1} .

EXPERIMENTAL.

The fact that iron is so easily and, at the same time, accurately determined by means of potassium permanganate, and that uranium solutions can be reduced, and then oxidized by potassium permanganate, suggested that possibly, with a few modifications, the Belohoubeck method could be adapted to the technical assay of uranium ores.

In order to demonstrate the best means of reducing uranium solutions, several different reducing agents were employed, the results of which are given below:

The first series of experiments was made by reducing the uranyl solution by means of zinc and sulphuric acid at boiling temperature, then by means of zinc and hydrochloric acid.

The second series was made by reducing the uranyl solution by means of strips of metallic aluminum, first in dilute sulphuric acid solutions, then in dilute hydrochloric acid solutions.

The third series was made by reducing the uranyl solutions by means of metallic magnesium, first in dilute sulphuric acid, then in dilute hydrochloric acid solutions.

The fourth series was made by passing the uranyl solutions through a long Jones' reductor.

The fifth series was made by reducing the uranyl solution by means of a strong solution of stannous chloride and destroying the excess of stannous chloride by adding sufficient mercuric chloride, as in the Zimmerman-Reinhart method, so largely used for the estimation of iron.

The standard solution of potassium permanganate was made by dissolving 18.96 grams of the salt in distilled water and diluting it to 6 liters, thus making a 0.01 normal solution. The standard was obtained by titrating ferrous sulphate solutions, containing a known quantity of iron.

$$1 \text{ cc. } \text{KMnO}_4 = 0.00548 \text{ gram iron.}$$

¹ Watts' "Chemical Dictionary," 4, 820.

The uranium standard was calculated from the iron standard by the proportion :

$$239.6 : 2 (55.9) = x : 0.00548; x = 0.01176.$$

Two equivalents of iron correspond to one equivalent of uranium, or the iron standard multiplied by 2.1425 gives the uranium standard. In order to get the uranium standard in terms of U_3O_8 , multiply the iron standard by 2.5243.

The standard of the permanganate solution was verified by taking a measured amount of standard uranium nitrate solution, and reducing it with about 50 grams of pure zinc and sulphuric acid (30 cc. sulphuric acid (sp. gr. 1.84) in 150 cc. of solution). The solution was diluted to 500 cc. and titrated. The results obtained agreed to the fifth decimal place with those of the iron titration.

TIKRATION OF URANIUM SOLUTIONS WITH POTASSIUM PERMANGA-NATE.

Zimmerman¹ recommends, when uranous solutions are titrated with standard potassium permanganate solution, that the permanganate be added in excess and the excess then titrated back with a standard solution of ferrous sulphate. He stated that by this procedure the oxidation of the uranous solution by air is prevented. In the following titrations—about sixty in number, and also a number of others made later—the recommendation of Zimmerman was not observed, but the uranous solution was titrated in the same manner as a ferrous solution. The oxidation of the uranous solutions was prevented by placing about 1 gram of dry sodium carbonate in the large Erlenmeyer flask in which the titrations were made. The mouth of the flask was closed by a $2\frac{1}{2}$ inch funnel, and the solution which was reduced in a small Erlenmeyer flask was emptied into it. The solutions, which were quite acid, on coming in contact with the dry sodium carbonate, liberated carbon dioxide which filled the "titration flask" and prevented the oxidation of the uranous solutions.

The reductions, whether made by metallic zinc, aluminum, or magnesium, were made in a small 250 cc. Erlenmeyer flask, the mouth of which was closed by a small funnel. The uranyl solutions were poured into the flask, acidified, the metal added, and the reduction carried on at boiling temperature. After the reduc-

¹ *Ann. Chem. (Liebig)*, 213, 300 (1882).

tion had occurred, the funnel and sides of the flask were washed down with distilled water and the hot solution rapidly emptied into the "titration flask" which contained about 1 gram of dry sodium carbonate. The flask in which the reduction was made was rinsed out four times with cold distilled water, the rinsings poured into the "titration flask," and the solution diluted to from 500 to 600 cc. The titrations were made at once, adding the permanganate solution till pink "end-point," which was very delicate, when sulphate solutions were titrated.

The determinations were made as follows: A measured amount of standard uranium nitrate solution was measured into a small beaker, and from 10 to 15 cc. of sulphuric acid (sp. gr. 1.84), added. The solution was evaporated to dense white fumes, allowed to cool, then poured into an Erlenmeyer flask, which contained a small amount of water. The solution was diluted to a definite volume (100 to 200 cc.) and more sulphuric acid added.

The best and most rapid reductions occurred when the amount of free sulphuric acid (sp. gr. 1.84) present was within the limits, 1 part acid to 4 parts solution, and 1 part acid to 5 parts solution. When the concentration is more than 1 to 4, the metal, especially zinc, is coated with a rather insoluble sulphate which retards the generation of hydrogen.

Comparing the time required for the complete reduction of uranyl solutions with that required for the reduction of iron solutions, it was found to be about twice as long, when equivalent amounts of uranium and iron salts were reduced.

When zinc was the metal used for generating the hydrogen, about 50 grams of pure metal (15 lumps) were used.

When the solutions were reduced by means of aluminum, fifteen strips of the metal were used, size 8 mm. wide by 15 mm. long, and 0.5 mm. thick.

The reductions by means of metallic magnesium were made by using eight pieces of a bar 8 mm. in diameter and 15 mm. long.

The reductions, whether made by means of metallic zinc, aluminum, or magnesium, were in all cases the same. The only difference noticed was the rapidity of solution of the metals; aluminum dissolved more rapidly than zinc, and magnesium more rapidly than aluminum. The reduction, whether carried on at boiling temperature for one hour, or for as long as five hours, did not go further than $\text{U}(\text{SO}_4)_2$. The time required for the reduc-

tion of about 0.1 gram of uranium by zinc is about one hour, for about 0.2 gram not less than one and a half hours. The uranyl sulphate solution, at first yellow in color, changes to light green and finally to green with bluish tinge, having the appearance of a dilute solution of nickel chloride, which color it retains even though the reduction be continued for as long as four hours.

The results, which were obtained by titrating uranous sulphate solutions, are all that can be desired, as they agree within analytical limits with those obtained by the standard gravimetric method, which is to precipitate the uranium with ammonia, and weigh it as U_3O_8 .

The reduction of hydrochloric acid solutions was also tried. For this purpose, a measured amount of standard uranium nitrate solution was twice evaporated to dryness with 10 cc. hydrochloric acid (sp. gr. 1.20). The dry mass of uranyl chloride was taken up with 15 cc. hydrochloric acid (sp. gr. 1.20), and water added, after which the solution was poured into a small Erlenmeyer flask and diluted to from 100 to 200 cc. More hydrochloric acid was added, and the solutions reduced at boiling temperature in the same manner as the sulphate solutions. The reductions were made first by the use of metallic zinc, then by metallic aluminum, and lastly by metallic magnesium. In all cases when the reduction was carried on for from two to four hours, it approached (and in several cases reached) the subchloride (U_2Cl_6 or UCl_4). With solutions of about 100 cc. volume and rather strongly acid (1 part hydrochloric acid (sp. gr. 1.20) to 4 parts solution), at boiling temperature the reduction to UCl_4 was complete within about two hours. By longer treatment the reduction went no further. The color of the hydrochloric acid solution of uranium, at first yellow, changed to green, to bluish green, to olive-green, and finally to reddish-brown—resembling the color of old port wine. The solutions, previous to titration, were cooled by running water, diluted to about 600 cc., and titrated in the same manner as the uranous sulphate solutions.

The "end-point" was not so delicate as when sulphate solutions were titrated. As no "preventative solution" was added, a small amount of chlorine was evolved after the solutions were allowed to remain standing for a few minutes. The interference of the "end-point" by chlorine was prevented by having a very small amount of free hydrochloric acid present, not over 3 per cent. of the total solution.

The results obtained are as follows :

REDUCTION OF URANYL SOLUTIONS BY METALLIC ZINC.

Experiment No.	Dilution at reduction. cc.	Time of reduction. Hours.	Dilution at the time of titration. cc.	Amount of free acid present. cc.	Amount of KMnO ₄ required. cc.	Uranium equivalent.	Theoretical amount of uranium taken.
1	100	2 $\frac{1}{4}$	600	15 H ₂ SO ₄	13.10	0.15406	0.15400
2	200	3	600	20 " "	13.15	0.15464	0.15400
3	125	1 $\frac{1}{2}$	500	20 " "	8.20	0.09643	0.09625
4	135	1 $\frac{1}{2}$	500	25 " "	8.20	0.09643	0.09625
5	130	1	600	20 " "	16.40	0.19286	0.19250
6	130	1	600	20 " "	16.35	0.19228	0.19250
7	125	1 $\frac{1}{2}$	500	20 " "	19.60	0.23050	0.23100
8	125	1 $\frac{1}{2}$	500	25 " "	19.65	0.23108	0.23100
9	100	2 $\frac{1}{4}$	600	30 HCl	21.10	0.15400
10	200	2 $\frac{1}{4}$	600	25 " "	19.80	0.15400

REDUCTION OF URANYL SOLUTIONS BY METALLIC ALUMINUM.

Experiment No.	Dilution at reduction. cc.	Time of reduction. Hours.	Dilution at the time of titration. cc.	Amount of free acid present. cc.	Amount of KMnO ₄ required. cc.	Uranium equivalent.	Theoretical amount of uranium taken.
11	110	1 $\frac{1}{2}$	600	15 H ₂ SO ₄	13.15	0.15464	0.15400
12	150	2 $\frac{1}{2}$	600	20 " "	13.05	0.15350	0.15400
13	150	2 $\frac{1}{2}$	600	20 " "	13.10	0.15406	0.15400
14	100	2 $\frac{1}{2}$	500	15 " "	13.05	0.15350	0.15400
15	100	3	500	15 " "	13.10	0.15406	0.15400
16	200	4	600	25 " "	13.15	0.15464	0.15400
17	120	1 $\frac{1}{2}$	600	30 " "	13.15	0.15464	0.15400
18	200	2 $\frac{1}{2}$	600	40 " "	13.10	0.15406	0.15400
19	200	2 $\frac{1}{2}$	600	50 " "	13.15	0.15464	0.15400
20	75	1 $\frac{1}{2}$	700	20 HCl	20.10	0.15400
21	75	1 $\frac{1}{2}$	700	20 " "	18.85	0.15400
22	200	3	700	20 " "	17.40	0.15400
23	200	3	700	20 " "	19.60	0.15400

REDUCTION OF URANYL SOLUTIONS BY METALLIC MAGNESIUM.

Experiment No.	Dilution at reduction. cc.	Time of reduction. Hours.	Dilution at the time of titration. cc.	Amount of free acid present. cc.	Amount of KMnO ₄ required. cc.	Uranium equivalent.	Theoretical amount of uranium taken.
24	125	1	600	20 H ₂ SO ₄	13.10	0.15406	0.15400
25	125	1	600	20 " "	13.05	0.15347	0.15400
26	125	2 $\frac{1}{2}$	700	20 HCl	16.90	0.15400
27	125	2 $\frac{1}{2}$	700	20 " "	17.60	0.15400

The reduction of uranyl solutions to the uranous state can also be made by passing the solution through a Jones reductor. The reductor used was much longer than those ordinarily employed for the reduction of iron solutions. It was made of a 50 cc. burette, in the lower part of which was placed an inch layer of broken glass and on top of this was poured an 18 inch column of 20 mesh amalgamated zinc. The amalgamation was done by washing the zinc with a warm dilute solution of mercurous nitrate, then thoroughly washing it with warm distilled water.

The determinations were made by taking a measured amount of standard uranium nitrate solution and evaporating it to dense white fumes with 10 cc. sulphuric acid (sp. gr. 1.84). The solution was allowed to cool, then diluted to from 100 to 150 cc. and more sulphuric acid added. The warm solution was poured through the reductor, and caught in a large Erlenmeyer flask which contained about 1 gram of dry sodium carbonate, and the mouth of which was closed by a small funnel. After all the solution had been emptied into the reductor, it was followed by about 250 cc. distilled water. The solution was then diluted to 500 cc., and titrated with 0.01 normal potassium permanganate solution to faint red end-reaction.

The time required for 100 cc. of uranyl solution and 250 cc. of water to pass through the reductor was about ten minutes; for 150 cc. uranyl solution and 250 cc. of water to pass through it required about twenty minutes.

Sutton¹ states that while washing the reductor free from iron solutions, the wash-water should be kept above the zinc level, so as not to allow of any air-spaces between the successive additions of water, in which case hydrogen peroxide is formed, thus causing high results. This caution was observed in the reductions.

The most satisfactory results were obtained when the ratio of free sulphuric acid (sp. gr. 1.84) to total solution was not less than 1 to 6, nor more than 1 to 5. When the solutions contained more acid than the ratio of 1 to 5, the zinc sulphate which formed did not go into solution, and prevented the ready passage of the solution through the reductor. When the acid was present in amounts less than the ratio of 1 to 7, the reduction of the solution was incomplete, due to too slow action of the acid on the zinc. The reduction was complete in all cases when the ratio of

¹ Sutton's "Volumetric Analysis," under "Iron."

free sulphuric acid (sp. gr. 1.84) to total solution was within the limits of 1 to 6 and 1 to 5. Even when the solutions were twice run through the reductor no further reduction occurred than when run through once.

The results obtained are shown in the table.

REDUCTION OF URANYL SOLUTIONS BY PASSING THROUGH REDUCTOR.

Experiment No.	Dilution at reduc-tion. cc.	Time of reduction. Minutes.	Dilution at the time of titration. cc.	Amount of free acid present. cc.	Amount of KMnO_4 required. cc.	Uranium equiv-ent.	Theoretical amount of ura-nium taken.
28	100	9	600	20 H_2SO_4	8.20	0.09643	0.09625
29	100	9	600	15 "	8.20	0.09643	0.09625
30	110	10	500	10 "	13.15	0.15404	0.1540
31	110	10	500	10 "	13.05	0.15347	0.1540
32	115	11	500	15 "	13.10	0.15406	0.1540
33	115	11	500	15 "	13.10	0.15406	0.1540
34	120	12	500	20 "	13.10	0.15406	0.1540
35	120	12	600	20 "	13.10	0.15406	0.1540
36	100	10	500	20 "	16.40	0.19286	0.1925
37	100	10	600	20 "	16.35	0.19228	0.1925
38	125	12	600	25 "	26.20	0.30810	0.3080
39	130	14	600	30 "	26.20	0.30810	0.3080
40	150	18	600	35 "	26.20	0.30810	0.3080
41	110	15	600	15 "	16.40	0.19286	0.1925
42	115	18	600	20 "	16.40	0.19286	0.1925
43	135	20	600	25 "	26.20	0.30810	0.3080

Solutions Nos. 41, 42, and 43 were twice passed through the reductor.

REDUCTION OF URANYL SOLUTIONS BY STANNOUS CHLORIDE.

These reductions were made in the same manner as iron by the Zimmerman-Reinhardt method. In some of the reductions the stannous chloride was allowed to act much longer than is ordinarily done for iron; but with the majority the procedure was the same as for iron reductions.

The color of the uranyl chloride solutions was yellow, but on continued boiling with stannous chloride it changed to green, and on still further boiling to reddish brown. When the solutions were boiled with stannous chloride, a small amount of dry sodium carbonate was added to the flask, the mouth closed by a small funnel, and the boiling continued.

When the reductions were allowed to continue for a minute or so, as for the reduction of ferric solutions, a very slight reduction occurred, but when the reduction was continued for from fifteen minutes to half an hour, the reduction approached and in several cases proceeded to the subchloride (UCl_3), the same as when a hydrochloric acid solution of uranium is reduced by either zinc, aluminum, or magnesium.

The uselessness of stannous chloride for the reduction of uranium solutions is shown by the following table:

REDUCTION OF URANYL SOLUTIONS BY STANNOUS CHLORIDE.

Experiment No.	Dilution at reduc-tion. cc.	Time of reduction. Minutes.	Dilution at the time of titration. cc.	Amount of free acid present. cc.	Amount of $KMnO_4$ used. cc.	Uranium equiva-lent.	Theoretical amount of ura-nium taken.
44	20	½	600	15	0.6–0.7	0.00823	0.1925
45							
46							
47							
48	75	½	500	20	0.8–1.5	0.01764	0.1925
49							
50	75	½	500	20	0.4–0.6	0.00706	0.1925
51							
52	35	1	550	35	0.8	0.00941	0.1925
53	50	1	550	45	2.0	0.02352	0.1925
54	35	5	600	35	16.0	0.18816	0.1925
55	50	5	600	45	18.5	0.21756	0.1925
56	75	10	600	10	4.0	0.04704	0.1925
57	75	10	600	10	8.5	0.09996	0.1925
58	35	10	600	25	11.0	0.12936	0.1925
59	30	10	600	15	15.5	0.18228	0.1925
60	30	15	600	15	20.9	0.24578	0.1925

PART III.—ESTIMATION OF URANIUM IN PITCHBLENDE.

In order to apply the preceding separations and determinations, to an actual technical assay of pitchblende, samples of the ore were analyzed by two entirely different methods: the Patera method with modifications, and the "ether extraction" method. In both cases the uranium was determined in several different ways. These assays gave an actual comparison of results, and at the same time tested the separations and estimations of uranium which were worked out on pure solutions.

The assays were first made by Patera's method as follows:

Eight samples of the finely divided ore (about 1.3 grams) were weighed into small beakers, and decomposed by adding 5 cc. water and 10 cc. nitric acid (sp. gr. 1.42). Complete solution was brought about by heating almost to boiling in covered beakers on a hot asbestos plate till the residues were almost white in color, then the watch-glasses were removed and the solutions slowly evaporated to a pasty mass. After cooling, the masses were taken up with 50 cc. water and 3 cc. nitric acid (sp. gr. 1.42), and the solution brought to boiling. The silica was filtered off and washed with boiling water and rejected. The filtrates were diluted to 200 cc. volume and hydrogen sulphide gas passed through the cold solutions for one hour. The precipitates of sulphides of lead, copper, etc., were filtered, washed with hydrogen sulphide water, and rejected. The filtrates from the sulphides were at first slowly heated, and finally boiled in order to expel hydrogen sulphide gas and to oxidize the iron. Evaporation was continued till the bulk of the solutions was about 125 cc., then the separated sulphur was filtered off and washed. The solutions were brought to boiling and 150 cc. of a saturated solution of sodium carbonate added, boiling was continued for twenty minutes, after which the precipitates (principally ferric hydroxide) were filtered off and washed three times by decantation and four times on the filter with hot water. The filtrates containing the uranium were evaporated to half volume (about 150 cc.), slowly neutralized with hydrochloric acid (sp. gr. 1.20) and about 3 cc. in excess, then boiled for half an hour till all carbon dioxide was expelled. The uranium was precipitated from the hot solutions by means of a slight excess of sodium hydroxide (free from carbonate), and boiling for about ten minutes, keeping the beakers covered with watch-glasses. The orange-yellow precipitates of sodium uranate were allowed to settle, the supernatant liquids poured through filters, and the precipitates twice washed by decantation and three times on the filters with hot water.

Precipitates Nos. 1 and 2, were dried in a hot oven, separated from the filters and ignited in platinum crucibles after which the ash of the papers was added to the crucibles and ignition continued at "redness" for five minutes. The residues on cooling were treated several times with hot water, after each treatment pouring the water through a small filter. The filters

were dried, ignited, added to the crucibles, and reignited at "redness" for ten minutes. After cooling in a desiccator, they were weighed. According to Patera, the residue consists of $\text{NaO}_2(\text{U}_2\text{O}_7)$, 100 parts of which contain 88.3 parts of U_2O_7 .

Precipitates Nos. 3, 4, 5, 6, and 7 were dissolved from the filters by warm dilute hydrochloric acid (sp. gr. 1.13), and caught in small beakers. The solutions were evaporated twice to dryness on a warm asbestos plate, the second time with 10 cc. hydrochloric acid (sp. gr. 1.20). The dry residues were taken up with 3 cc. hydrochloric acid, diluted to 100 cc., and brought to boiling. The silica, dissolved from the beakers by the strong alkali solution, was filtered off, and washed with boiling water.

Solutions Nos. 3 and 4 were brought to boiling, 5 cc. hydrochloric acid (sp. gr. 1.20) added, and ammonia (sp. gr. 0.90) in excess. The solutions were boiled for fifteen minutes, thus changing the voluminous amorphous precipitate of yellow ammonium uranate into a more crystalline form, darker in color, which was readily and rapidly washed. The precipitates were allowed to settle, the supernatant liquids poured through filters, and the precipitates washed three times by decantation and twice on the filter with a hot dilute solution of ammonium chloride (2 grams of salt to 100 cc. water). The precipitates were dried, placed in platinum crucibles together with filter-paper, and slowly ignited till the paper was completely destroyed, then ignited in a blast-flame for ten minutes, after which they were slowly cooled in a gradually decreasing Bunsen flame. During ignition the crucibles were placed in a slanting position in order to allow of free circulation of air in the crucible, thus obtaining complete oxidation to U_2O_7 . They were allowed to cool in a desiccator, and weighed.

Solution No. 5 was diluted to 150 cc., brought to boiling, and 5 cc. hydrochloric acid (sp. gr. 1.20) added. The solution was neutralized with ammonia (sp. gr. 0.90) and 5 cc. added in excess. Acetic acid was slowly added to the hot solution, stirring all the while, till the yellow precipitate disappeared. The uranium was then precipitated by means of ammonium dihydrogen phosphate, adding about twice as much as was necessary for complete precipitation. The solution was boiled for fifteen minutes, allowed to cool, then filtered, and the precipitate washed four times on

the filter with a hot 2 per cent. solution of ammonium chloride. The precipitate was dried, separated from the filter-paper which was first ignited in a porcelain crucible, after which the precipitate was added and ignited at low redness for ten minutes over a Bunsen flame. The crucible was allowed to cool, the residue moistened with a few drops of nitric acid (sp. gr. 1.42), dried on a hot plate, and reignited at low redness for ten minutes. The lemon-yellow colored precipitate of uranyl pyrophosphate ($(\text{UO}_2)_2\text{P}_2\text{O}_7$) was weighed, and the U_3O_8 equivalent obtained by multiplying the weight by 0.66815.

Solutions Nos. 6 and 7 were evaporated to about 30 cc. volume allowed to cool, 30 cc. sulphuric acid (sp. gr. 1.84) added, and evaporation continued to dense white fumes. The solutions were poured into 250 cc. Erlenmeyer flasks, diluted to 150 cc., and reduced at boiling temperature by about 50 grams of pure granulated zinc. The reductions were continued for one and a half hours till the solutions were a clear green color. The solutions were then poured into a large Erlenmeyer flask, which contained about one gram of dry sodium carbonate, diluted to 500 cc. and titrated by 0.01 normal potassium permanganate solution.

Precipitate No. 8, of sodium uranate, was dissolved from the filter with warm dilute nitric acid (1 part acid (sp. gr. 1.42) and 2 parts water) and caught in a small beaker. The solution was evaporated to dryness twice, the second time with 10 cc. nitric acid (sp. gr. 1.42). The dry mass was taken up with 5 cc. of 50 per cent. acetic acid, diluted to 50 cc., and the solution boiled till all salts were dissolved. The silica, which was dissolved from the beaker by the strong sodium carbonate solution, was filtered off and washed with hot water. The solution was diluted to exactly 100 cc. in a graduated flask, 50 cc. were measured into a large clean platinum dish and the uranium determined by electrolysis as follows: Added 0.5 gram sodium acetate, diluted to 125 cc. and electrolyzed at a temperature of 65° to 75° C., with a current of $\text{N.D.}_{100} = 0.8$ to 1.0 ampere. The uranium was completely precipitated, as hydrated protosesquioxide, within eight hours. The electrolyte was emptied into a beaker, and the black deposit washed with warm water. The electrolyte and the washings were poured through a fluted filter-paper, the paper several times rinsed with hot water, dried, and ignited on the cover of a platinum crucible, and the ash added to the dish. The dish was

then dried, ignited over a blast-lamp for ten minutes, and allowed to cool in a gradually decreasing Bunsen flame. It was placed in a desiccator and, after thoroughly cooling, was weighed. The ignited deposit consisted of U_3O_8 .

The results obtained by this series of assays are as follows :

Experiment No.	Amount of ore taken. Grams.	Weighed as :	Weight. Gram.	Calculated to U_3O_8 equivalent.	Per cent. of U_3O_8 .	Average per cent.
1	1.2863	$\text{NaO}(\text{U}_3\text{O}_8)_2$	0.3064	0.27055	21.03	20.76
2	1.3278	$\text{NaO}(\text{U}_3\text{O}_8)_2$	0.3071	0.27117	20.49	
3	1.2882	U_3O_8	0.2616	0.26160	20.31	
4	1.2880	U_3O_8	0.2653	0.26530	20.60	20.46
5	1.2840	$(\text{UO}_2)_2\text{P}_2\text{O}_7$	0.3297	0.25940	20.20	20.20
6	1.4004	Titrated	...	0.29090	20.77	
7	1.2164	Titrated	0.24940	20.50	20.63
8	0.6416	U_3O_8	0.1306	0.13060	20.36	20.36

Estimation of Uranium in Pitchblende by the Ether Extraction Method.—The ether extraction method differs from the Patera method in that the uranium is not separated from the fourth group members by means of sodium carbonate, but by ether and by ammonium carbonate. The iron was separated from uranium and the other metals by shaking the hydrochloric acid solution with ether, free from alcohol. The uranium was then separated from the other associated metals (aluminum, manganese, zinc, and nickel) by means of ammonium carbonate.

The procedure was as follows: Seven samples (about 1.3 grams) of the finely divided pitchblende were decomposed with boiling dilute nitric acid (1 part acid (sp. gr. 1.42) and 1 part water) till the residues which remained were almost white in color. The solutions were then evaporated to a pasty mass, taken up with 15 cc. hydrochloric acid (sp. gr. 1.20), and evaporated to dryness twice, the second time with 10 cc. hydrochloric acid (sp. gr. 1.20). The salts were taken up with 5 cc. hydrochloric acid (sp. gr. 1.20), diluted to 150 cc., brought to boiling, and the silica filtered off and washed. The filtrates were diluted to 250 cc. and the lead, copper, etc., precipitated as sulphides by passing hydrogen sulphide gas through the cold solutions for about an hour. The filtrates from the sulphides were evaporated slowly to about 150 cc., and boiled for a few minutes in order to expel all hydrogen

sulphide. The separated sulphur was filtered off and washed. The solutions were brought to boiling, 5 cc. nitric acid (sp. gr. 1.42) added, and boiling continued till the iron was completely oxidized, after which ammonia (sp. gr. 0.90) was added in excess and boiling continued for fifteen minutes. The precipitates of impure ferric hydroxide, ammonium uranate, etc., were filtered off and washed with a warm 2 per cent. solution of ammonium chloride. The wet precipitates were dissolved from the filters with warm dilute hydrochloric acid (sp. gr. 1.10) and caught in small beakers. The solutions were twice evaporated to dryness, the second time with 10 cc. hydrochloric acid (sp. gr. 1.20). The dry salts were taken up with 15 cc. hydrochloric acid (sp. gr. 1.10), the beakers covered with watch-glasses, and the solutions heated till all salts had dissolved but not long enough to lose any of the acid by evaporation. After cooling, the solutions were emptied into 250 cc. separatory funnels, and the beakers rinsed out four times with 5 cc. hydrochloric acid (sp. gr. 1.10). Fifty cc. of pure ether, which had previously been shaken up with hydrochloric acid (sp. gr. 1.10), were added to each funnel, and thoroughly shaken for about seven minutes with the aqueous hydrochloric acid solutions, occasionally relieving the pressure, due to evaporation of ether. After agitation, the funnels were allowed to stand for a few minutes till the two solutions separated, then the lower aqueous layers were run into other separatory funnels. The ether layers, containing most of the iron, were twice shaken up with 5 cc. hydrochloric acid (sp. gr. 1.10) and the washings added to the main solutions containing the uranium. The second extractions were made with 50 cc. ether, and the third with 30 cc. ether. In both cases the ether solutions were twice washed with 5 cc. hydrochloric acid (sp. gr. 1.10). The aqueous hydrochloric acid solutions, now free from iron, contained a small amount of ether, which was allowed to evaporate spontaneously by exposure. They were then evaporated to about half volume (40 cc.), diluted to 100 cc., nearly neutralized with ammonia, and 100 cc. of a saturated solution of ammonium carbonate added, which precipitated all the metals except uranium. The solutions were slowly boiled for five minutes, filtered, and the precipitates washed with hot water. The filtrates were evaporated to half volume in order to get rid of most of the carbon dioxide. Yellow precipitates of ammonium

uranate separated during boiling, and were dissolved by acidifying the solutions with hydrochloric acid. The solutions were again boiled for about half an hour longer, and the uranium determined in four different ways as outlined below.

Solutions Nos. 9 and 10 were precipitated with ammonia in the same manner as solutions Nos. 3 and 4 and the uranium weighed as U_3O_8 .

Solutions Nos. 11 and 12 were precipitated by an excess of ammonium dihydrogen phosphate the same as solution No. 5, and the uranium weighed as $(\text{UO}_2)_2\text{P}_2\text{O}_7$.

Solutions Nos. 13 and 14 were evaporated with sulphuric acid, reduced by metallic zinc and titrated by potassium permanganate as described under Nos. 6 and 7.

In solution No. 15, the filtrate from the ammonium carbonate precipitation was evaporated to dryness with nitric acid, and the uranium determined electrolytically as already described under No. 8.

The results obtained by the ether extraction method are as follows:

Experiment No.	Amount of ore taken.	Weighted as:	Weight. Gram.	Calculated to U_3O_8 equivalent.	Per cent. of U_3O_8	Average per cent.
9	1.2405	U_3O_8	0.2565	0.2565	20.67	20.61
10	1.2409	U_3O_8	0.2550	0.2550	20.55	
11	1.2390	$(\text{UO}_2)_2\text{P}_2\text{O}_7$	0.3233	0.2545	20.54	
12	1.2991	$(\text{UO}_2)_2\text{P}_2\text{O}_7$	0.3431	0.2701	20.79	20.66
13	1.2892	Titration	0.2672	20.80	
14	1.2828	Titration	0.2646	20.63	20.71
15	0.6207	U_3O_8	0.1283	0.1283	20.67	20.67

A comparison of these results with those obtained by the Patera separation shows greater uniformity here. The close agreement is proof not only of the superiority of the ether extraction method, but also of the accuracy of the methods of determination of uranium already described.

SUMMARY OF RESULTS.

The conclusions drawn from this investigation on the separation and determination of uranium, briefly stated, are as follows:

1. In order to separate uranium (and the other members of

group 4) from the metals of groups 5 and 6, the solution should contain not over one part of concentrated acid (either hydrochloric or nitric acid) in fifty parts of solution.

2. The separation of uranium from the metals of groups 3 and 4 is best accomplished by means of either a saturated solution of sodium carbonate, or else by ether followed by a saturated solution of ammonium carbonate. The latter method is preferable when the introduction of fixed alkalies and silica is undesirable.

3. The ether extraction method for the separation of uranium from iron depends on the fact that ferric chloride is extracted from an aqueous hydrochloric acid solution, whereas the uranyl chloride is retained in the aqueous solution. For this separation it is necessary that the hydrochloric acid used for the solution be of 1.10 specific gravity and that three ether extractions be made. The ether used should be free from alcohol, and also previously shaken up with hydrochloric acid (sp. gr. 1.10).

4. The separation of uranium from iron by means of sodium carbonate is complete, provided a large excess of a saturated solution of sodium carbonate be used, and the solution boiled for at least fifteen minutes after the precipitation. The boiling is necessary in order to get all the uranium into solution. By such treatment, no uranium remains with the iron, which is completely precipitated as ferric hydroxide in a form readily filtered and washed.

5. The separation of uranium from the alkalies and alkaline earths by means of electrolysis is complete, easily accomplished and gives accurate results.

6. The separation of uranium from the alkalies and alkaline earths is accomplished by precipitating the uranium three times from a hot solution with ammonia in the presence of ammonium chloride.

7. The separation of uranium from the alkalies and alkaline earths by means of an excess of ammonium phosphate in the presence of ammonium acetate is complete. The precipitations should be made from a hot solution and the boiling continued for at least fifteen minutes.

8. The yellow slimy amorphous precipitate of an ammonium uranate, formed by precipitating uranium with ammonia in the presence of an ammonium salt, is converted into a darker crystalline form by boiling it for about twenty minutes, and then allowing it to settle in the cold.

9. The separation of the filter-paper from the precipitate of ammonium uranate for the purpose of igniting to UO_2 or U_2O_5 is unnecessary.

10. The complete oxidation of uranium to U_2O_5 is accomplished by igniting ammonium uranate, in either a platinum or porcelain crucible, over a blast-lamp. This is done by having the crucible in a slanting position and igniting intensely over a blast-lamp for about ten minutes, after which the crucible is allowed to cool in a slowly decreasing Bunsen flame.

11. The reduction of U_2O_5 to UO_2 , as recommended by Rose for the purpose of control, was found unreliable.

12. The estimation of uranium as phosphate is easily and accurately done when the precipitant used is ammonium phosphate, in the presence of ammonium acetate. The precipitate of $\text{UO}_2\text{NH}_4\text{PO}_4$ on boiling becomes crystalline, and is easily filtered and washed. The ignited precipitate previous to weighing should be moistened with nitric acid (sp. gr. 1.42), dried and reignited at low redness in a porcelain crucible. Above this temperature, and especially so in platinum, a reduction of the $(\text{UO}_2)_2\text{P}_2\text{O}_7$ always occurs. Whenever this happens it may be reoxidized to $(\text{UO}_2)_2\text{P}_2\text{O}_7$ by moistening the greenish mass with nitric acid (sp. gr. 1.42) and reigniting at low redness. The ignitions should be done in porcelain.

13. The most rapid determination of uranium is accomplished by reducing a sulphate solution by means of pure metallic zinc and titrating it with standard potassium permanganate solution in an atmosphere of carbon dioxide. The reductions, whether made by means of metallic zinc, aluminum, magnesium, or in a long Jones reductor, were in all cases complete, and the results obtained were concordant with those obtained gravimetrically.

14. When hydrochloric acid solutions of uranium are reduced by means of metallic zinc, aluminum or magnesium, the reduction goes lower than UCl_4 . It approached and in several cases reached the subchloride UCl_3 . When stannous chloride is used the results are utterly unreliable; so no reduction of uranium in an hydrochloric acid solution can be used for the estimation of uranium.

This work was suggested by Dr. Edmund H. Miller, and carried out under his direction.

METHODS OF STANDARDIZING ACID SOLUTIONS.

BY CYRIL G. HOPKINS.

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THE recent articles on "The Preparation of an Exact Standard Acid" and "The Electrolysis of Copper Sulphate as a Basis for Acidimetry," by Higgins¹ and Kohn,² respectively, both of whom appear to have overlooked the fact that this electrolytic method for standardizing acids was introduced by Hart and Croasdale³ more than ten years ago, have suggested that a series of results obtained by the writer, in a comparative study⁴ of "Methods of Standardizing Reagents Used in Acidimetry and Alkalimetry," would add something of interest and value on the subject, especially to such as are interested in volumetric analysis.

The special object in this study was to determine the most exact method of standardizing a solution of acid for subsequent use as "standard acid," this being the ultimate and practical purpose of any basis for acidimetry.

Six different methods of standardizing acid solutions were investigated and compared:

1. The silver chloride method of standardizing hydrochloric acid with some modifications and improvements as to manipulation.
2. The method of standardizing sulphuric acid by weighing as ammonium sulphate, as recommended by Wenig.⁵
3. The method of using metallic sodium, introduced by Hartley⁶ and improved by Neitzel.⁷
4. The method of standardizing acids by use of pure crystallized borax.
5. The method based upon the electrolysis of copper sulphate, introduced by Hart and Croasdale⁸ and strongly recommended by Hart⁹ and recently rediscovered by Kohn.¹⁰

¹ *J. Soc. Chem. Ind.*, **19**, 958 (1900).

² *Ibid.*, **19**, 962 (1900).

³ *J. Anal. Chem.*, **4**, 424 (1890).

⁴ Author's unpublished thesis for the degree of Master of Science, Cornell University, 1894. Acknowledgment is made of valuable suggestions from Dr. G. C. Caldwell, under whose supervision this work was done.

⁵ *Ztschr. angew. Chem.*, (1892), 204.

⁶ *Quar. Jour. Chem. Soc.*, **26**, 123 (1873).

⁷ *Ztschr. anal. Chem.*, **32**, 422 (1893).

⁸ *J. Anal. Chem.*, **4**, 424 (1890).

⁹ *Ibid.*, **6**, 421 (1892).

¹⁰ *J. Soc. Chem. Ind.*, **19**, 962 (1900).

6. The method of standardizing oxalic acid by means of metallic iron and potassium permanganate.

Before the details of the results obtained in this work are considered, it is desired to call attention to two questions which have important effects upon accuracy in different methods of standardizing :

1. Is the method of standardizing direct or indirect?
2. Is the actual error which may be made in the determination of the substance which is brought to the balance mathematically increased or diminished by computing to the equivalent amount of the acid standardized?

In considering the first question a classification may be made of (1) direct, (2) indirect, and (3) doubly indirect methods, the direct methods requiring only a gravimetric determination, the indirect requiring a gravimetric and a volumetric determination, or a weighing and a titration, and the doubly indirect methods requiring one weighing and two titrations.

The silver chloride and ammonium sulphate methods are direct, the chlorine being precipitated and weighed as silver chloride, and the sulphuric acid being neutralized and weighed as ammonium sulphate.

The metallic sodium and borax methods are indirect, the sodium and the borax each being weighed and then, after being put in solution, titrated to standardize the acid.

The copper sulphate and iron-permanganate methods are doubly indirect, each requiring one weighing and two titrations. The copper is deposited and weighed, the small amount of sulphuric acid liberated titrated against an alkaline solution, and this in turn titrated to standardize the permanent acid solution. The iron is likewise weighed, then put into solution, titrated against permanganate solution, and this solution titrated against the oxalic acid.

To answer the second question we must compare the weight of the substance which is brought to the balance with the weight of the equivalent (but not equal) amount of the standard acid. In all of the methods, one of the numbers from which the strength of the standard acid is calculated is obtained by using the balance. The substance weighed is our real basis for computation. In the two direct methods it is silver chloride and ammonium sulphate; in the indirect methods it is sodium and borax, and in the doubly

indirect methods it is copper and iron. The accuracy of the manipulation and the purity of the substance are important factors in obtaining correct weights of these substances, and the ratio which a given quantity of the weighed substance bears to the equivalent amount of the acid standardized is an important consideration. Following is a tabular statement arranged to show a comparison of these ratios in the six methods, the numbers being determined by the reactions in each case and reduced to the basis of monobasic acid :

Substances weighed.	Equivalent weights of acid.	Ratios existing.
143.39 AgCl	36.46 HCl	I : 0.25
66.10 $(\text{NH}_4)_2\text{SO}_4$	49.04 H_2SO_4	I : 0.74
23.06 Na	36.46 HCl	I : 1.58
191.15 $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	36.46 HCl	I : 0.19
31.80 Cu	{ 49.04 H_2SO_4 36.46 HCl	I : 1.54 I : 1.15
56.00 Fe	45.01 $\text{H}_2\text{C}_2\text{O}_4$	I : 0.80

From this table it can be seen that an error of 1 mg. in the purity or in the manipulation in securing the weight of the sodium would cause an error of 1.58 mg. in the equivalent amount of standard hydrochloric acid; while the same error, 1 mg., in obtaining the weight of borax would cause an error of only 0.19 mg. in the equivalent amount of standard acid. In other words, an error of 1 mg. in obtaining the weight of sodium would have the same influence on the accuracy of the determination of the strength of the standard acid as would an error of 8.3 mg. in obtaining the weight of borax, equivalent amounts of each (sufficient to neutralize the same quantity of acid) being taken. Similarly, 1 mg. error in obtaining the weight of copper would have the same influence on standard sulphuric acid as would an error of 6.2 mg. in the weight of silver chloride on standard hydrochloric acid. These are certainly considerations which should be taken into account, as they may very materially affect the possible accuracy of methods.

Following are statements of results obtained by each method with as brief descriptions as seem practicable of processes of manipulation :

1. *Silver Chloride Method.*—Standardizing hydrochloric acid by precipitating with silver nitrate and weighing the silver chloride.

A solution of hydrochloric acid of about one-fourth normal strength was prepared for standardizing. Portions of the acid solution were measured out with a pipette, the exact capacity of which was found by calibration with mercury to be 50.06 cc. The solution was delivered into a 250 cc. Erlenmeyer flask provided with a clean, smooth, close-fitting, solid rubber stopper, the pipette being rinsed with a few cubic centimeters of pure water (which was added to the measured acid), and then dried before again being used. All measurements were reduced¹ to a uniform temperature of 20° C.

A sufficient quantity (as determined by stoichiometric computation) of a 5 per cent. solution of silver nitrate to nearly, but not quite completely, precipitate all of the chlorine, was at once added, the necessary additional quantity being added in less than 1 cc. portions. The flask was closed with a rubber stopper² and shaken after each addition, so that the precipitate would settle and it could easily be known when sufficient precipitant had been added, a large excess of silver nitrate, which would possess some solvent action on the silver chloride and necessitate much washing for its complete removal from the precipitate, thus being avoided.

After the precipitation was complete, the flask was shaken until, after standing a short time, the supernatant liquid became perfectly clear. It was then allowed to stand in an inclined position until the precipitate settled down quite compactly in the bend of the flask. The solution was then poured off through a Gooch crucible as completely as possible without transferring more than a mere trace of the precipitate. The flask was then set aside in an inclined position, such that the precipitate was not at the lowest point, where the remaining liquid would collect. After two or three minutes the liquid, which had drained out of the precipitate, was also poured through the filter. About 100 cc. of pure water containing a trace of nitric acid,³ sufficient only to make it distinctly acid, were now poured into the flask, which was then closed and thoroughly shaken, the precipitate allowed to settle, and the liquid twice decanted just as before. This

¹ Schulze: "Expansion of Liquids in Glass Vessels," *Ztschr. anal. Chem.*, 21, 167 (1882).

² Whenever the stopper is removed it must, of course, be carefully rinsed off into the flask.

³ In perfectly pure water, silver chloride does not cohere well, but remains persistently in very fine particles; indeed, after it has been well collected in large particles by being shaken in an acid solution, it will separate again into fine particles if shaken with pure water.

treatment was repeated with another 100 cc. of the wash-water, after which the precipitate was again shaken with the wash-water and then transferred to the crucible. The last traces are quickly and easily and completely transferred, simply by the use of a good "spritz" bottle, the flask being inclined mouth downward over the crucible and rotated during the operation. The "transfer" wash-water gave no test for silver.¹ The precipitate was heated in the air-bath at 130° to 150° to constant weight.

Six determinations gave the following results:

Solution taken. cc.	Temper- ature.	AgCl found. Gram.	AgCl from 50.06 cc. at 20°. Gram.	HCl in 1 cc. at 20°. mg.
1 50.06	20.0°	1.9310	1.9310	9.808
2 50.06	20.0°	1.9312	1.9312	9.809
3 50.06	23.5°	1.9295	1.9310	9.808
4 50.06	23.5°	1.9292	1.9307	9.807
5 50.06	22.0°	1.9301	1.9309	9.808
6 50.06	22.0°	1.9301	1.9309	9.808

Another solution of hydrochloric acid of slightly greater strength was subsequently standardized by using the method just described, and in doing this work an attempt was made to determine the exact loss of silver chloride (if there be any loss) incurred by this method of washing. In the following determinations, Nos. 1, 2, 3, and 4 were washed exactly as described above, while Nos. 5 and 6 were washed just five times as much by exactly the same method of washing. Regularly three portions of 100 cc. each of liquid are decanted from the precipitate, and the precipitate is then transferred with a 100 cc. portion of wash liquid; but in Nos. 5 and 6 (below) this fourth 100 cc. portion was also decanted each time until the last of the five complete washings, when, of course, it was used in transferring the precipitate. Furthermore, in order that the solvent action of the five complete washings should produce an effect equal to five times the effect of the one necessary washing, an addition of 1 cc. of the silver nitrate solution was made to the first 100 cc. of wash-water used in each of the four extra washings.

¹ When working with duplicates this method of washing by thorough decantation takes little extra time, and not more than 1 or 2 cc. of liquid will be left in the precipitate. The excess of silver nitrate solution added in the precipitation contains only about 50 mg. of silver nitrate, and the volume of liquid, when the precipitation is complete, is at least 100 cc. Suppose that 5 cc. of this remains with the precipitate after shaking and decanting; by theory this should retain only 2.5 mg. of silver nitrate. After the second 100 cc. is decanted, about 0.1 mg. of silver nitrate would be left in the flask, and, after the third decantation, only 0.005 mg., an unweighable quantity, of silver nitrate would remain with the silver chloride precipitate. The fact that not a trace of silver was found in the wash-water after the transfer of the precipitate proves this theory correct in practice.

Six determinations gave the following results:¹

	HCl in 1 cc. at 20°. Mg.
1.....	10.297
2.....	10.295
3.....	10.296
4.....	10.295
5.....	10.297
6.	10.292

The results show that there is certainly no appreciable loss of silver chloride by this process of washing.

These twelve results (in two sets) include all of the determinations which were made by the method just described; in other words, all results obtained are here reported. These results and seven years of subsequent experience² with the method lead me to confidently assert that by this method a skilled manipulator can easily and quickly make determinations of hydrochloric acid within a limit of error of 0.5 mg. of silver chloride on 2 grams of precipitate.

2. *Ammonium Sulphate Method.*—Standardizing sulphuric acid by neutralizing the acid solution with ammonium hydroxide, evaporating to dryness, and weighing the ammonium sulphate. This was first recommended in 1892 by M. Wenig.³

A solution of about one-fourth normal sulphuric acid was used. Portions of 50.06 cc. were measured out and delivered into a weighed platinum dish. Ammonium hydroxide was then added in slight excess, the solution evaporated to dryness on the water-bath, and the residue dried to constant weight at 120°.

The ammonium hydroxide was distilled just before using. The sulphuric acid was free from nitrogen and the residue of ammonium sulphate was completely volatile upon gentle ignition, showing the absence of fixed bases.

Six determinations of the sulphuric acid in the standard solu-

¹ These figures are taken from a copy of the thesis already referred to. The laboratory note-book in which the full record of the determinations was preserved has been subsequently lost in a fire, hence the complete data, including weights of silver chloride, etc., cannot be given.

² The following are duplicate determinations on four different solutions of hydrochloric acid which have been standardized in the course of ordinary work (weights of silver chloride are given):

	1. Grams.	2. Grams.	3. Grams.	4. Grams.
AgCl found { 1	1.4103	1.4062	1.2173	1.2296
{ 2	1.4104	1.4064	1.2177	1.2295

³ *Ztschr. angew. Chem.*, 1892, p. 204.

tion were made by this method, with the following results (in No. 2 a slight mechanical loss of ammonium sulphate occurred):

Solution taken. cc.	Temperature.	(NH ₄) ₂ SO ₄ found. Gram.	(NH ₄) ₂ SO ₄ from 50.06 cc. at 20°. Gram.	H ₂ SO ₄ in 1 cc. at 20°. mg.
1 50.06	19.5°	0.7808	0.7807	11.570
2 50.06	19.5°	0.7795 (?)	0.7794 (?)	11.549 (?)
3 50.06	20.5°	0.7806	0.7807	11.570
4 50.06	20.5°	0.7809	0.7810	11.574
5 50.06	19.0°	0.7809	0.7807	11.570
6 50.06	19.0°	0.7808	0.7806	11.569

No. 2 being omitted, these weights of ammonium sulphate from 50.06 cc. of solution, at 20°, agree within 0.4 mg. on nearly 0.8 gram of residue and they indicate that this method of standardizing sulphuric acid is exceedingly accurate. The method is certainly simple and rapid. A comparison of the results obtained by this and the other methods is given below.

3. *Sodium Method.*—Standardizing acids by the use of metallic sodium.

The use of metallic sodium as a basis for acidimetry was first recommended in 1873 by Hartley.¹ In 1893 Neitzel² suggested that the sodium be weighed under petroleum in a small beaker instead of in weighing-tubes as recommended by Hartley.

I found a small glass-stoppered weighing-bottle to be an improvement over the beaker, as the petroleum is appreciably volatile at the ordinary temperature. The petroleum was distilled over sodium before being used, that portion being taken which distilled above 200°.

The sodium was cut out as rapidly as possible from a block of the metal, a piece with clean metallic surfaces being thus obtained. With a pair of forceps, it was quickly placed into a weighing-bottle containing sufficient petroleum to cover it. After being weighed, the sodium was dissolved in neutral alcohol in an Erlenmeyer flask which was connected with a reflux condenser. The solution was diluted with water (poured in through the condenser tube) and then titrated against standard acid.

Phenolphthalein was used as an indicator, giving a very sharp and satisfactory "end-reaction."

The burette used was carefully calibrated and the burette readings were taken to hundredths of a cubic centimeter as accurately as possible.

¹ *Quar. J. Chem. Soc.*, 26, 123 (1873).

² *Ztschr. anal. Chem.*, 32, 422 (1893).

Six determinations gave the following results :

	Metallic sodium taken. Gram.	Acid (HCl) solution required. cc.	Tempera- ture.	Acid solu- tion required at 20°. cc.	Acid solution at 20° required for 0.7154 gram sodium. ¹ cc.	HCl in 1 cc. at 20°. mg.
1	0.8853	142.10	23.5°	142.00	114.75	9.857
2	0.6358	101.95	23.5°	101.88	114.63	9.867
3	0.9352	150.45	27.0°	150.21	114.91	9.843
4	0.7004	112.40	26.0°	112.25	114.65	9.865
5	0.6229	100.00	22.0°	99.96	114.80	9.853
6	0.5128	82.47	23.0°	82.42	114.98	9.837

As standardized by the silver method (average of six determinations) this acid contained in 1 cc. 9.808 mg. hydrochloric acid.

The following two determinations (only) were made to standardize the sulphuric acid solution by use of metallic sodium. The results follow :

	Metallic sodium taken. Gram.	Acid (H ₂ SO ₄) solution required. cc.	Tempera- ture.	Acid solu- tion required at 20°. cc.	Acid solution at 20° required for 0.5145 gram sodium. ² cc.	H ₂ SO ₄ in 1 cc. at 20°. mg.
1	0.4750	86.85	23°	86.80	94.01	11.637
2	0.5539	101.25	23°	101.19	93.98	11.641

As standardized by the ammonium sulphate method (average of the five trustworthy determinations) this acid contained in 1 cc. 11.571 mg. sulphuric acid.

It will be observed that the results obtained by the sodium method, with both hydrochloric and sulphuric acids, agree well among themselves, considering that they are obtained by an indirect method which includes volumetric determinations. But it will also be observed that the results obtained by the sodium method are invariably higher than those obtained by the silver chloride and the ammonium sulphate methods. Without doubt this discrepancy is due to impurities contained in the sodium itself. Traces of carbon and iron were easily detected, and the presence of potassium was revealed by the spectroscope. The presence of elements of higher equivalent weights than sodium was indicated by converting the metal to sulphate. Two determinations gave 3.0783 and 3.0781 grams sulphate per gram of metal taken, while by theory 1 gram sodium is equivalent to 3.0829 grams sodium sulphate. Iron and potassium would each

¹ Average amount taken. The number of cubic centimeters given in this column are computed for each separate determination to show in cubic centimeters the limit of error in the titrations.

² See previous foot-note.

retain a smaller proportion of sulphuric acid radical than would sodium, while the carbon would be oxidized and lost.

Although the sodium used in this work was shown to be not perfectly pure and its titrating value to be not absolutely correct, so that results of the highest exactness could not be obtained by using the sodium as a substance with which to standardize acids, nevertheless its titrating value was, of course, constant whether used against hydrochloric or sulphuric acid; and, by considering the strength of the standard sulphuric acid as determined by the ammonium sulphate method, the relation found between the sulphuric acid and sodium, and that found between the sodium and the hydrochloric acid, we have all the necessary data for computing the strength of the hydrochloric acid determined by a doubly indirect method (based upon the ammonium sulphate determinations), independent of the silver method or the sodium method.

By using the average of the five satisfactory determinations of sulphuric acid, and the average of the two titrations of the sulphuric acid against sodium and then computing through the six separate titrations of sodium against hydrochloric acid, I obtain the following values (column 1) for 1 cc. of the hydrochloric acid solution (column 2 gives the results obtained by the direct silver chloride method, and column 3 those obtained by the regular sodium method).

HCl IN 1 CC. SOLUTION AT 20°.

	^{1.} Doubly indirect ammonium sulphate method.	^{2.} Direct silver chloride method.	^{3.} Indirect sodium method.
1	9.799	9.808	9.857
2	9.809	9.809	9.867
3	9.785	9.808	9.843
4	9.807	9.807	9.865
5	9.793	9.808	9.853
6	9.780	9.808	9.837

It is interesting to observe that, within the limits of error in titration, the results which are based upon the ammonium sulphate method are in perfect agreement with those obtained by the direct silver chloride method.

4. *Borax Method.*—Standardizing acids by the use of crystallized borax.

This method is recommended by Rimbach,¹ by whom the

¹ Ber. d. chem. Ges., 26, 171 (1893).

method was also employed in his work on the atomic weight of boron.¹

In the following work, C. P. borax was dissolved in water by the aid of heat. As the solution cooled, crystals began to form at about 45°. When the temperature had fallen to 30°, the mother-liquor was drained off, the crystals washed with cold water, placed on drying paper, and dried at the room temperature for four days, being turned occasionally to insure thorough drying. To standardize an acid, the crystallized borax is simply weighed, dissolved in water, and titrated against the acid. The standard hydrochloric acid mentioned as having been standardized by the silver chloride method and found by six closely agreeing determinations to contain 10.295 mg. hydrochloric acid in 1 cc. at 20°, was used in this work.

Ten determinations by means of borax were made, four after four days' exposure to the air, four after five days', and two after six days' exposure, the titrations always being made with the hydrochloric acid solution at 20°. Litmus, as recommended by Salzer,² was used as an indicator in the first four titrations; but the end-reaction was not sharp, and in the subsequent titrations dimethyl orange, as Rimbach recommends, was used. It was very satisfactory.

	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ taken. After four days. Grams.	Acid required at 20° cc.	Acid solution at 20° required for 5.4944 grams borax. ³ cc.	HCl in 1 cc. at 20°. mg.
1	5.3481	99.1	101.81	10.294
2	5.5075	102.1	101.86	10.289
3	5.3044	98.4	101.92	10.282
4	5.2896	98.1	101.90	10.284
After five days.				
5	5.4370	101.05	102.13	10.263
6	5.5977	104.05	102.13	10.262
7	5.4045	100.37	102.04	10.271
8	5.4906	102.05	102.12	10.262
After six days.				
9	5.2891	98.60	102.43	10.231
10	6.2754	117.05	102.47	10.226

Although the results obtained on one and the same day agree well with themselves, especially when dimethyl orange was used as the indicator; yet the results indicate that the borax is not

¹ *Ber. d. chem. Ges.*, **26**, 164 (1893).

² *Ztschr. anal. Chem.*, **32**, 529 (1893).

³ Average amount taken.

constant, but that it continually loses water of crystallization. To test this point further, samples of the borax which had been dried by exposure to the air for six days were weighed out and allowed to stand, exposed to the air but protected from the dust.

Following are the weights of the two samples on several subsequent days :

No. of days drying.	Weight of borax.	
	1. Grams.	2. Grams.
6	9.2214	10.0762
7	9.2132	10.0646
9	9.1920	10.0396
10	9.1738	10.0135

It is evident that the borax continually lost water of crystallization whether exposed to the air on drying paper or kept in open vessels. Rimbach found that crystallized borax remained constant after three or four days' drying, if kept in the air at the ordinary temperature, but that it lost weight readily when placed in dry air. Of course if the temperature and humidity of the air were such that the vapor-pressure of the atmospheric moisture exceeded that of crystallized borax, then the salt would not effloresce ; and Rimbach may possibly have worked under such conditions.

Copper Sulphate Method.—Standardizing acids by use of the sulphuric acid set free in the electrolysis of copper sulphate. This method was introduced by Hart and Croasdale¹ in 1890. It consists in subjecting a solution of pure copper sulphate to electrolysis, weighing the copper deposited, titrating the liberated acid against an alkaline solution, and then using the alkali in standardizing a permanent acid solution. It is thus a doubly indirect method.

In the following work platinum dishes were used for the negative electrodes. The strength of current used corresponded to about 3.5 cc. of oxyhydrogen gas per minute. The acid set free was titrated against approximately one-tenth normal solution of sodium hydroxide made from metallic sodium. The alkali was then titrated against standard hydrochloric acid.

The copper sulphate was tested for acidity with methyl orange and found to be perfectly neutral. Tests for other bases than copper gave negative results. After the liberated acid had been

¹ *J. Anal. Chem.*, 4, 424 (1890).

transferred and the platinum dish well rinsed with pure water, the deposited copper was washed with absolute alcohol and the dish dried at the temperature of the hands, excepting in determinations 1 and 2, in which the alcohol was drained out well and the last traces burned out as directed by Hart and Croasdale. In determination 2, some of the copper turned bluish green, indicating the formation of a salt of copper combined with some intermediate acid product of combustion. Because of this fact No. 2 is not considered a trustworthy determination.

Because of the large influence on the accuracy of the final results of any error in weighing the copper the weights were all taken by the method of oscillations.¹ The relation between the standard hydrochloric acid and the sodium hydroxide solutions was determined by titration as follows :

1	50.06 cc. acid required	119.37 cc. alkali.
2	50.06 "	" 119.45 "
3	50.06 "	" 119.41 "
Average 1	" "	2.3853 cc. alkali.

Following are the results of eight determinations of the strength of a standard hydrochloric acid as ascertained by means of the copper sulphate method :

	Copper deposited from CuSO ₄ . Gram.	NaOH solution required to neutralize the liberated H ₂ SO ₄ . cc.	HCl solution equivalent at 20°. cc.	HCl in 1 cc. at 20° mg.
1	0.15349	42.85	17.964	9.796
2	0.16664 (?)	45.78	19.192	9.954 (?)
3	0.15596	43.45	18.216	9.793
4	0.14853	41.35	17.336	9.823
5	0.16719	46.58	19.528	9.815
6	0.14921	41.57	17.428	9.816
7	0.16468	45.80	19.201	9.833
8	0.19207	53.68	22.505	9.785

The following table gives a series of results obtained by Hart and Croasdale² in standardizing a solution of sulphuric acid by this method, and, for comparison, the results of my own determinations as just given (except that they are reduced to 0.5 cc. acid solution to make the results more comparable, my acid being very much stronger than theirs); and also my results obtained on the same acid solution by the direct silver chloride method, and on a

¹ Kohlrausch's "Physical Measurements," p. 23, (1891).

² *J. Anal. Chem.*, 4, 426 (1890).

sulphuric acid solution by the ammonium sulphate method (also reduced to 0.5 cc.).

Hart and Croasdale. Copper sulphate method, H_2SO_4 in 1 cc. mg.	Hopkins. Copper sulphate method, HCl in $\frac{1}{2}$ cc. mg.	Hopkins. Silver chloride method, HCl in $\frac{1}{2}$ cc. mg.	Hopkins. Ammonium sulphate method, H_2SO_4 in $\frac{1}{2}$ cc. mg.
4.814	4.898	4.904	5.785
4.802	4.897	4.905	5.785
4.791	4.912	4.904	5.787
4.799	4.908	4.904	5.785
4.819	4.908	4.904	5.785
4.811	4.917	4.904
4.767	4.893
Maximum variation } 0.052	0.024	0.001	0.002

The copper sulphate method of standardizing acids gives fairly satisfactory results, but it falls far short of the direct silver chloride and ammonium sulphate methods in accuracy. The reason for this is found both in the substances used and in the number of manipulations. First, the ratio of the substance weighed to the acid determined is such that an error in obtaining the weight of copper vitiates the final result five or six times as much as an equal error in weighing silver chloride, and twice as much as an equal error in weighing ammonium sulphate. Further, the amount of copper which can be conveniently deposited in suitable condition for washing and weighing is relatively and absolutely smaller than the amounts of silver chloride or of ammonium sulphate conveniently manipulated. But the still more serious objection to the method is the fact that, even after the weight of copper is obtained, two volumetric determinations are necessary before the strength of the permanent acid solution can be ascertained.

In a second paper¹ on "Copper Sulphate as a Material for Standardizing Solutions," Dr. Hart appears to have overlooked these objections, as may be seen from the following quotation:

"A committee of the Association of Official Agricultural Chemists have compared our method (Hart and Croasdale's method) with others, and speak well of it. I doubt whether their report adds to the evidence in either direction, however, since their ultimate standard was a solution of hydrochloric acid, the strength of which was determined with silver nitrate. Every chemist

¹ *J. Anal. Appl. Chem.*, 6, 421 (1892).

knows, however, that it is an easy matter to make an error of half a milligram in any method involving a precipitation and the transfer of a precipitate; Croasdale's results and those of Richards show that the error involved is much less when copper is determined by the battery method, and that we can probably determine copper more accurately than any other element, consequently that our method should be taken as the standard and others referred to it."

No question need be raised in regard to the exactness of the electrolytic assay of copper. It is a direct and absolute method for the determination of copper, but the method, based upon that determination, of using the liberated acid for standardizing a permanent acid solution by making two volumetric determinations, and computing from the low equivalent weight of copper (as compared with that of silver chloride) is very indirect and not exceedingly accurate; and this comparative study of methods of standardizing acids has convinced the writer that the objections mentioned to the copper sulphate method are applicable and valid; also that the silver chloride method (as described) and the ammonium sulphate method are extremely accurate and satisfactory for standardizing solutions of hydrochloric and sulphuric acids, respectively.¹

UNIVERSITY OF ILLINOIS.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 32.]

SOME EXPERIMENTS WITH THE MONONITROORTHOPHTHALIC ACIDS.

BY MARSTON TAYLOR BOGERT AND LEOPOLD BOROSCHEK.

Received August 1, 1901.

ALTHOUGH both mononitro-*o*-phthalic acids have long been well known, yet, of their derivatives, with the exception of their salts and esters, only the anhydride, imide, and anil have been described. It seemed, therefore, of interest to prepare some of the other derivatives of these acids and to study their properties, and the present paper records our first experiments along this line.

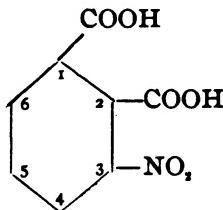
¹ The iron-permanganate method gave fairly accurate results as a method for standardizing oxalic acid. It is no more indirect and no less accurate (if the purity of the iron be known) than the copper sulphate method. It is thought that a detailed description here of the work done upon the iron-permanganate method would not be of special interest or value.

Naturally, the first question to be decided was as to the best method for the preparation of the pure acids themselves. Our experience has shown that the direct nitration of phthalic acid itself, or of its anhydride, gives good yields of the pure 3, nitro-*o*-phthalic acid, but that as a method for the preparation for the isomeric 4, nitro acid it is not so good as that depending upon the oxidation of β -nitrophthalide with alkaline potassium permanaganate.

Of the derivatives of the 3, nitro-*o*-phthalic acid, we have prepared and studied the acid aniline and *o*-toluidine salts, a new acid ethyl ester, the imide, amide, amidic acid, ethylimide, anil, anilic acid, ortho-, meta-, and paranitranils, ortho-, meta-, and paratolils, and the hydrazide.

Of the 4, nitro-*o*-phthalic acid, the following derivatives are described: Acid aniline salt, a new acid ethyl ester, anhydride, imide, amide, amidic acid, ethylimide, anil, anilic acid, ortho-, meta-, and paranitranils, ortho-, meta-, and paratolils, β -tolilic acid, and hydrazide; also the corresponding azophthalic acid and azophthalide.

By the action of phosphorus pentachloride upon the anhydride of the 3, nitro-*o*-phthalic acid, the anhydride of the 3, chlor-*o*-phthalic acid was formed, and from this the free acid and imide were prepared.



α , OR 3, NITRO-*o*-PHTHALIC ACID.

Preparation of the Acid.

*Method of Beilstein and Kurbatow.*¹—One part of α -nitronaphthalene is dissolved in 7 parts of 90 per cent. acetic acid, and 5 parts of chromic anhydride gradually added. When the reaction is over, dilute with water, filter out unchanged nitronaphthalene, extract the filtrate with chloroform, to remove nitrophthalide, boil the acetic acid solution with barium carbonate, decompose

¹ *Ann. Chem. (Liebig)*, 202, 217 (1880).

² *Ber. d. chem. Ges.*, 18, 3452 (1885).

the precipitated barium nitrophthalate with sodium carbonate, acidify with sulphuric acid, collect the liberated nitrophthalic acid in ether, evaporate the ether, and crystallize the residue from water.

We have found this method unsatisfactory for several reasons. In the first place, the reaction proceeds with considerable violence, prohibiting the use of large amounts of materials, while attempts to moderate its violence only result in the formation of more resinous by-products, as was likewise the experience of Beilstein and Kurbatow;¹ yet, in spite of the apparent energy of the reaction, considerable of the nitronaphthalene is recovered unchanged, in some cases as much as 25 per cent. Then, the method is rather long and tedious, the yield small (25 per cent. of theory) and the quality of the resulting acid poor, the crystals invariably showing a low melting-point and carrying a small amount of a red coloring-matter from which they are freed with difficulty.

*Method of Miller.*²—This is the process generally employed for the simultaneous preparation of both nitro-*o*-phthalic acids. It is as follows:

Fifty grams of *o*-phthalic acid are nitrated in a roomy flask by a mixture of 75 grams concentrated sulphuric acid and 75 grams fuming nitric acid, the flask being heated two hours upon the water-bath. The result of this nitration is a mixture of the two nitro-*o*-phthalic acids and picric acid, together with unchanged phthalic acid, acetic acid, etc. Towards the close of the heating some of the 3,nitro acid begins to separate in prisms. The mass is then allowed to cool and is precipitated by the addition of water. The composition of the precipitate varies with the amount of water added, as the two nitro-*o*-phthalic acids possess very different solubilities in dilute mineral acids: 240 cc. of water precipitate mainly the 3,nitro acid, while half this amount throws down the 4,nitro acid also. This difference in solubility cannot, however, be used as a means of separation (for the 4,nitro acid, at least), since picric acid remains in solution with the 4,nitro acid and combines with it in recrystallization; hence, it is better to precipitate both nitrophthalic acids together, although some picric acid is thus always carried down, apparently in union with the 4,nitro acid. The reaction mixture is, therefore, diluted

¹ *Loc. cit.*

² *Ann. Chem. (Liebig)*, 208, 223 (1881).

with 120 cc. of water, allowed to stand twelve hours in a cool place, the precipitate filtered out upon cloth, and the acid mother-liquor removed as completely as possible by suction and pressure. The precipitate is then rubbed up with a little water and extracted repeatedly with ether. The first ether extracts contain mainly the 4,nitro acid and picric acid, and are, therefore, yellow in color, while the more difficultly soluble 3,nitro acid is extracted last. Evaporation of the ether leaves a yellow acid mixture, melting at $154^{\circ}-186^{\circ}$, in a yield of 85 per cent. of the theory, from which the 3,nitro acid may be obtained by frequent crystallization from water, the 4,nitro acid and picric acid remaining in the mother-liquors. The yield of pure 3,nitro acid thus obtained is about 50 per cent. of the weight of the crude acid mixture.

As pointed out by Miller,¹ this process can be considerably shortened if it is not desired to recover the 4,nitro acid, by taking the first precipitate of crude acids, removing the mineral acids by careful washing, pressing, and draining upon a clay plate, and then separating the difficultly soluble 3,nitro acid by crystallizing this cake repeatedly from water.

In carrying out this method, the phthalic acid dissolves after about a half hour's heating, to a clear amber solution, with evolution of copious fumes of oxides of nitrogen. After heating for about an hour longer, the 3,nitro acid begins to crystallize out, and the contents of the flask soon change to a mass of crystals. Sufficient water is then added to precipitate mainly the 3,nitro acid, the mixture is allowed to stand twenty-four hours in a cool place, and the precipitate then separated as thoroughly as possible from the acid mother-liquor, giving a cake of crude 3,nitro acid. This is dissolved in hot water and the solution concentrated until crystals begin to separate from the hot liquid. It is then allowed to cool slowly and is left four or five hours in a cool place. Most of the 3,nitro-*o*-phthalic acid is thus separated in small hard transparent crystals of a faint yellowish cast, which are further purified by recrystallization from water, the yield then being about 30 per cent. of the theory.

As there is usually some unnitrated phthalic acid in the first precipitate of crude acids, this precipitate was subjected to a second nitration in similar manner. Only a small amount of the crude acid then dissolved in the hot nitrating solution, showing the

¹ *Ber. d. chem. Ges.*, II, 393 (1878).

presence of but little phthalic acid. The yield of 3,nitro acid was increased by this second nitration to about 32 per cent. of that theoretically obtainable from phthalic acid.

Method of May,¹ Edinger² and Leupold.³—This is quite similar to that of Miller, except that phthalic anhydride is used instead of the acid.

As might be expected from the smaller amount of water present in this reaction, the precipitation of the nitro acids begins much sooner, and after an hour's heating upon the water-bath the mixture in the flask is a nearly solid mass of crystals. This rapid separation of the nitro acids seems to prevent complete nitration, as the yield of pure 3,nitro acid by this process was only about 25 per cent. of the theory, while a renitration raised this figure to nearly 38 per cent. It is quite possible that by the careful addition of water during the first nitration the separation of the nitro acids could be retarded, thereby increasing the yield and obviating the necessity for a second nitration.

In renitrating the crude nitro acids no complications need be feared from formation of dinitrophthalic acids, as Beilstein and Kurbatow⁴ have shown that it is exceedingly difficult to further nitrate 3,nitro-*o*-phthalic acid.

The nitration of phthalic acid or of its anhydride thus readily gives good yields of pure 3,nitro-*o*-phthalic acid, and it is the method by which we have prepared the acid for conversion into the derivatives described later.

As thus prepared, 3,nitro-*o*-phthalic acid forms hard transparent prisms, of a very pale yellow color. Its behavior when heated resembles that of the unsubstituted phthalic acid; in an open tube, it decomposes at 207°, or lower, into water and the anhydride, the point at which this decomposition begins depending upon the rapidity of the heating, while in a sealed tube it melts at 222° (corr.). It is quite readily soluble in hot water, much less so in cold; easily soluble in cold acetone; moderately soluble cold, easily hot, in methyl or ethyl alcohols, and ethyl acetate; sparingly soluble in cold isoamyl alcohol, moderately in hot; difficultly soluble in ether; nearly insoluble in petroleum ether, benzene, chloroform, carbon tetrachloride, ethyl nitrate,

¹ Inaug. Dissertation, Freiburg, (1880).

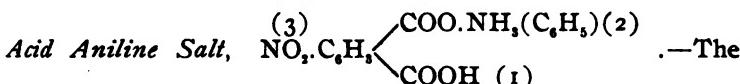
² *J. prakt. Chem.*, (2), 53, 382 (1896).

³ Inaug. Dissertation, Basle, (1897).

⁴ *Loc. cit.*

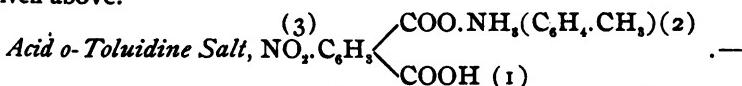
carbon bisulphide, benzene, and nitrobenzene; glacial acetic acid, at 26°, takes up 7.5 per cent. (Aguiar,¹ Diehl and Merz).² It is much less soluble in all ordinary solvents than the corresponding 4-nitro-*o*-phthalic acid.

*Derivatives of 3, Nitro-*o*-phthalic Acid.*

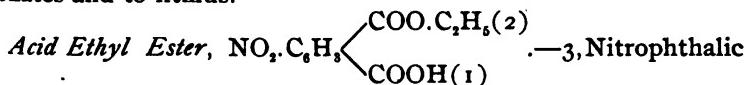


strong tendency of 3, nitro-*o*-phthalic acid to form acid salts, with the ammonium bases, rather than neutral salts, was commented upon by Laurent³ as early as 1842. This peculiarity is still more marked in the case of the aromatic amines, of which no neutral salts with the nitrophthalic acids are known. By adding aniline to the alcoholic solution of 3, nitro-*o*-phthalic acid and then concentrating upon the water-bath, colorless needles of the acid aniline salt separate, melting at 185°–187°, with loss of water and production of the anil. Only the acid salt could be obtained, no matter how large the excess of aniline employed. Several months after the completion of this experiment an article by Graebe and Buenzod⁴ appeared, in which they record similar results.

As the carboxyl adjacent to the nitro group is the stronger of the two, it seems most likely that this acid salt has the formula given above.



Prepared in a similar manner, this acid salt forms fine white needles melting at 181°, a few degrees above which point it breaks up into water and the *o*-tolil. Its aqueous solution is acid to carbonates and to litmus.



anhydride was dissolved in absolute alcohol in a flask carrying a reflux condenser, and the solution heated for five hours upon the water-bath. Upon distilling off the alcohol, a yellow oil remained, which was dissolved in strong sodium carbonate solution and the mixture extracted with ether, to remove any neutral

¹ *Ber. d. chem. Ges.*, 5, 899 (1872).

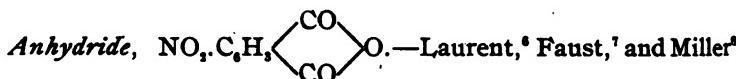
² *Ibid.*, 11, 1667 (1878).

³ *Ann. Chem. (Liebig)*, 41, 110 (1842).

⁴ *Ber. d. chem. Ges.*, 32, 1992 (1899).

ester (none was found). The addition of hydrochloric acid to the sodium carbonate solution caused the separation of a white crystalline precipitate, melting at 157° , soluble in alcohol or ether, but insoluble in cold water. Its solutions decompose carbonates and are acid to litmus. The substance was dissolved in alcohol and titrated with tenth-normal sodium hydroxide solution. 0.807 gram of the substance took 33.3 cc. of the tenth-normal sodium hydroxide; theory requires 33.7 cc. The silver salt forms nearly colorless crystals.

The isomeric acid ethyl ester, with the ester group meta to the nitro, and melting at 110° , was first obtained (in the impure state) by Faust,¹ and, subsequently described by Baeyer,² Miller,³ Nerking,⁴ and Edinger.⁵



all state that the anhydride is formed by the action of heat upon the acid. Recently, however, Lipschitz⁹ reported that by careful heating of the acid at 220° , even in a stream of carbon dioxide, he obtained only a brown melt containing decomposition products with the odor of nitrogen dioxide and benzaldehyde. Our experience has been more in accord with that of the earlier investigators. The 3-nitro acid, in a small flask, was heated in an oil-bath at 235° – 240° until water vapor ceased to be given off (six to eight hours' heating necessary). On cooling, a yellow crystalline solid appeared, which was nearly pure anhydride, and, after a single crystallization from glacial acetic acid or acetone, formed colorless needles melting sharply at 163° . If there should be any indication of unchanged acid in the product, it may be crystallized from acetyl chloride, which likewise converts the acid to the anhydride.¹⁰ The anhydride is easily soluble in acetyl chloride or hot glacial acetic acid, moderately in acetone or hot alcohol, and very difficultly soluble in benzene.

¹ *Ann. Chem.* (Liebig), 160, 57 (1871).

² *Ber. d. chem. Ges.*, 10, 125, 1079 (1877).

³ *Ann. Chem.* (Liebig), 208, 223 (1881).

⁴ *Inaug. Dissertation*, Heidelberg, (1896).

⁵ *J. prakt. Chem.*, (2), 53, 382 (1896).

⁶ *Ann. Chem.* (Liebig), 41, 110 (1842).

⁷ *Ztschr. Chem.* 1869, 108; *Ann. Chem.* (Liebig), 160, 57 (1871).

⁸ *Ann. Chem.* (Liebig), 208, 223 (1881).

⁹ *Monatsh. Chem.*, 21, 787 (1900).

¹⁰ Leupold: *Loc. cit.*; Lipschitz: *Loc. cit.*

Imide, $\text{NO}_2\text{C}_6\text{H}_3(\text{CO})_2\text{NH}$.—Laurent¹ states that when the

ammonium salt of 3, nitro-*o*-phthalic acid is distilled the free acid is regenerated and no imide is formed; also, that when the anhydride is treated with dry ammonia gas a new compound is obtained, but he gives none of the properties of this "new compound." We have, therefore, prepared this imide by the action of heat upon the acid ammonium salt. The salt begins to decompose at about 225° , and the heating is continued until no more water vapor is evolved and the melt remains in quiet fusion. On cooling, a yellow crystalline solid is obtained, easily soluble in acetone, moderately in hot alcohol or hot glacial acetic acid, and very difficultly in water. It crystallizes from alcohol in pale yellow lustrous needles melting at 215° – 216° .

- I. 0.1513 gram substance gave 20 cc. nitrogen at 22° and 753 mm.
 II. 0.1694 gram substance gave 22.1 cc. nitrogen at 22° and 751.5 mm.

	Calculated for $\text{C}_8\text{H}_4\text{O}_4\text{N}_2$.	Found.
	I.	II.
Nitrogen.....	14.62	14.82 14.51

By dissolving the imide in a mixture of alcohol and acetone and adding exactly one molecule of potassium hydroxide dissolved in alcohol, a white crystalline precipitate of the potassium salt of the imide results.

Amide, $\text{NO}_2\text{C}_6\text{H}_3(\text{CO.NH}_2)_2$.—Strong ammonium hydroxide

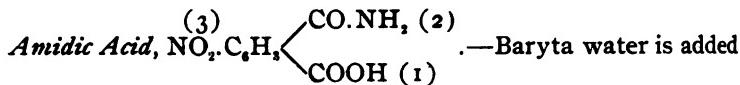
is added to the imide and the mixture warmed slightly. The lustrous flaky crystals of the imide gradually disappear and in their place a sandy crystalline precipitate appears, the reaction being complete at the end of about one hour. Dried to constant weight over sulphuric acid *in vacuo*, the following analytical results were obtained from the substance :

- 0.1452 gram substance gave 26.1 cc. nitrogen at 22° and 758 mm.

	Calculated for $\text{C}_8\text{H}_7\text{O}_4\text{N}_3$.	Found.
Nitrogen.....	20.1	20.3

When heated in an open tube, the amide melts at 200° – 201° with evolution of ammonia, remelting, after cooling, at 215° , the melting-point of the imide.

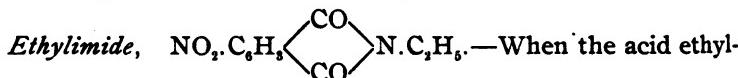
¹Loc. cit.



to the imide and the mixture heated for an hour at 80° , and then allowed to stand for twenty-four hours at the ordinary temperature. Upon acidifying with sulphuric acid, the barium sulphate precipitate carries down with it some of the amic acid, which may be recovered by extraction with cold strong alcohol. Concentration of the filtrate from the barium sulphate precipitation, or of the alcoholic extracts, yields white needles of the amidic acid. This concentration must be carried out cold, by blowing a stream of dry air through the liquid, as hot concentration appears to destroy the amic acid, probably causing hydration. The crystals of amic acid were washed with ether, and dried *in vacuo* over sulphuric acid. They melt at 156° , with evolution of water, and, after solidifying, remelt at 213° , showing the production of the imide. The amidic acid is but sparingly soluble in cold water, easily in alcohol, and apparently insoluble in ether. Its solutions are acid to litmus and decompose carbonates.

0.1509 gram substance gave 17.6 cc. nitrogen at 22° and 755 mm.

	Calculated for $\text{C}_8\text{H}_5\text{O}_3\text{N}_2$.	Found.
Nitrogen.....	13.3	13.13

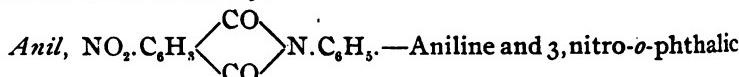


amine salt is heated at 125° - 165° for some time there results a greenish crystalline solid, sparingly soluble in hot water, but easily in hot alcohol. From the latter solvent it crystallizes in long lustrous needles of yellowish cast, melting at 105° .

0.1747 gram substance gave 20.4 cc. nitrogen at 27.5° and 760 mm.

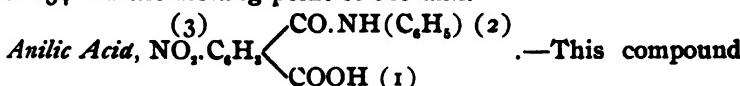
	Calculated for $\text{C}_{10}\text{H}_8\text{O}_4\text{N}_2$.	Found.
Nitrogen.....	12.7	12.85

Attempts to prepare the same compound by the action of ethyl iodide upon the potassium salt of the imide, in sealed tubes, all resulted unsatisfactorily.



anhydride are heated together at about 190° , or, better, the acid aniline salt is carefully heated. In the latter case, an amber colored solid is obtained, soluble in acetone, difficultly soluble in

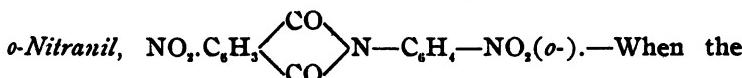
cold alcohol, moderately in hot. Crystallized from a mixture of alcohol and acetone, it forms yellowish needles, melting at 136° – 137° . Graebe and Buenzod,¹ whose article, as already explained, appeared subsequent to the completion of this part of the work, give 134° as the melting-point of the anil.



may be prepared from the anil in a manner entirely analogous to that for the preparation of the amic acid from the imide, except that when the baryta solution is acidified by sulphuric acid most of the anilic acid separates with the barium sulphate as a flocculent precipitate, which must be dissolved out by cold alcohol, and the solution concentrated cold as already described. Pale yellow needles are thus obtained, which can be washed with ether and dried. These needles melt at 180° , and, after resolidifying, the melting-point sinks to 135° , showing conversion of the anilic acid to the anil (m. p. 136°). The anilic acid is easily soluble in alcohol, difficultly in cold water, and apparently insoluble in ether. Its solutions are acid to litmus but do not seem to decompose carbonates.

0.1962 gram substance gave 17.4 cc. nitrogen at 23° and 758 mm.

	Calculated for C ₁₄ H ₁₀ O ₂ N ₂ .	Found.
Nitrogen.....	9.8	9.96



When the acid *o*-nitraniline salt is heated it begins to decompose at 150° with loss of water, and at 200° the last portions of water are removed. The yellowish mass resulting, when crystallized from a mixture of alcohol and acetone, gives yellow crystals of the *o*-nitranil, melting at 167° .

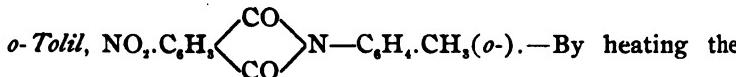
0.1619 gram substance gave 20 cc. nitrogen at 25° and 759 mm.

	Calculated for C ₁₄ H ₁₀ O ₂ N ₂ .	Found.
Nitrogen	13.4	13.7

m-Nitranil is prepared by heating the acid *m*-nitraniline salt at 170° – 200° . The product is less soluble in alcohol or acetone than the corresponding ortho compound, and, when crystallized from a mixture of these solvents, forms pale brown, microscopic crystals, melting at 219° .

¹ *Loc. cit.*

p-Nitranil.—The acid *p*-nitraniline salt was heated at 200°–250° until water ceased to be evolved. The brown crystalline mass resulting was purified by crystallization from acetone, in which it was only moderately soluble, small yellow crystals of the *p*-nitranil being thus obtained, of a melting-point of 249°.



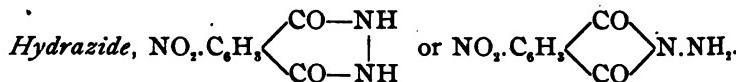
acid *o*-toluidine salt at 160°–190°, and crystallizing the product from a mixture of alcohol and acetone, pale yellow needles of the *o*-tolil result, melting at 145°. These are easily soluble in acetone, and only sparingly in alcohol.

m-Tolil is prepared in a similar manner, the acid *m*-toluidine salt losing its water at about the same temperature as the ortho compound. From a mixture of alcohol and acetone, it crystallizes in long yellow needles, melting at 129°.

p-Tolil.—Equal molecules of *p*-toluidine and 3, nitro-*o*-phthalic anhydride were heated together at 170°–180° until the evolution of water ceased. The *p*-tolil thus obtained crystallizes from a mixture of alcohol and acetone in pale yellow needles (m. p. 154°).

0.2003 gram substance gave 18.3 cc. nitrogen at 23° and 752 mm.

	Calculated for $\text{C}_{15}\text{H}_{10}\text{O}_4\text{N}_2$.	Found.
Nitrogen.....	9.93	10.17



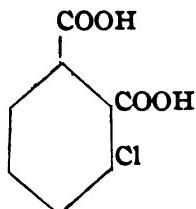
—3, Nitro-*o*-phthalic acid was dissolved in alcohol, one molecule of hydrazine hydroxide (in 50 per cent. aqueous solution) added, and the solution evaporated to dryness. The residue was then carefully heated in an oil-bath. At 150° the evolution of water began and continued until the temperature reached 250°. Even at this latter temperature the material did not melt, but remained a pale brown, porous solid. It dissolved readily in a warm sodium carbonate solution, with effervescence, forming a yellowish red liquid. Acidification with hydrochloric acid caused the precipitation of a yellow powder, which crystallized from glacial acetic acid in pale yellow, microscopic crystals, melting with decomposition at about 320°. These crystals are likewise decomposed by caustic alkali.

0.1510 gram substance gave 27.4 cc. nitrogen at 24° and 761 mm.

Calculated for $C_8H_5O_4N_2$.

Found.

Nitrogen	20.3	20.36
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3, Chlor-o-phthalic Acid.

Anhydride, $Cl.C_6H_3\begin{array}{c} CO \\ \swarrow \quad \searrow \\ CO \end{array}O$.—Ten grams of 3,nitro-o-phthalic

anhydride and 11 grams phosphorus pentachloride were heated together in a sealed tube for six hours at 175°. From the contents of the tube pale yellow crystals were separated, which, after recrystallization from a mixture of benzene and naphtha, formed nearly colorless needles, melting at 122°, corresponding to that recorded by Krüger¹ for 3,chlor-o-phthalic anhydride.

0.1763 gram substance gave 0.1415 gram silver chloride.

Calculated for $C_8H_5O_3Cl$.

Found.

Chlorine	19.4	19.8
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Acid, $Cl.C_6H_3\begin{array}{c} COOH \\ \swarrow \quad \searrow \\ CO \end{array}COOH$.—By boiling the anhydride obtained

above for several hours with dilute hydrochloric acid, the corresponding chlorphthalic acid was obtained. This crystallized from water in colorless needles (m. p. 186°). Guareschi² found the melting-point of 3,chlor-o-phthalic acid to be 184°.

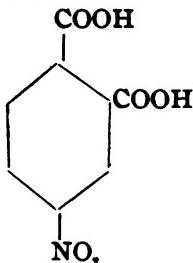
Imide, $Cl.C_6H_3\begin{array}{c} CO \\ \swarrow \quad \searrow \\ CO \end{array}NH$.—The 3,chlor-o-phthalic anhydride

was dissolved in strong ammonium hydroxide, the solution evaporated to dryness, and the residue carefully heated. A sublimate of white needles resulted. In an open tube, these needles sublime before melting; in a closed tube they melt at 118°-120°. The substance appears to be the 3,chlorphthalimide, which has

¹ Ber. d. chem. Ges., 18, 1759 (1885).

² Gaz. chim. ital., 17, 120.

not been previously described, but not sufficient of the substance was prepared for an analysis.



β, OR 4, NITRO-*o*-PHTHALIC ACID.

Preparation of the Acid.

*Method of Miller.*¹—As has been stated, the action of a mixture of concentrated sulphuric acid and fuming nitric acid upon phthalic acid produces about equal amounts of the two nitro-*o*-phthalic acids. Of these, the 3,nitro acid is readily separated in the pure state by virtue of its sparing solubility in water. The isolation of the 4,nitro acid, however, is a matter of much greater difficulty, not only on account of its great solubility, but also from the fact that the picric acid present tends to follow it through and to combine with it or its salts in crystallization, so that even by the recrystallization of its difficultly soluble barium salt only about 15 per cent. pure 4,nitro acid can be recovered from the original precipitate of crude acids. A much better method of separation depends upon the fact that when a mixture of these two acids is esterified by the action of hydrochloric acid gas upon their alcoholic solution the 3,nitro acid yields mainly the acid ester, while the 4,nitro acid is converted into the neutral ester. By treating the product of this esterification with strong sodium carbonate solution, the acid ester (together with picric acid) is dissolved out, leaving the neutral ester of the 4,nitro acid as an insoluble oil.

In applying this process, we usually crystallized out as much of the 3,nitro acid as possible from the crude nitro acids, then evaporated the mother-liquors to dryness, dissolved the residue in absolute alcohol and esterified with dry hydrochloric acid gas. Upon the addition of water, then, the esters separate as an oily layer, which is washed repeatedly with strong sodium carbonate

¹ *Ber. d. chem. Ges.*, 11, 393 (1878); *Ann. Chem. (Liebig)*, 208, 223 (1881).

solution. The neutral ester of the 4,nitro acid is thereby left as an oil, which gradually solidifies, and is purified by crystallization from ether and then from alcohol, forming large pale yellow plates, melting at 34° - 35° . From this neutral ester the free acid may be prepared by saponifying with alcoholic potassium hydroxide, dissolving the precipitated potassium salt in water, acidifying the solution with hydrochloric acid and extracting with ether. Evaporation of the ether leaves the 4,nitro-*o*-phthalic acid as a crystalline crust, melting at 162° .

Although the yield by this process is good, the purification of the neutral ester is rather troublesome, as it is apt to contain small amounts of the neutral esters of 3,nitro-*o*-phthalic acid and of phthalic acid itself, the presence of the latter preventing the solidification of the oily ester.

Preparation of the Acid from p-Nitrophthalide.—Hoenig¹ was the first to prepare the 4,nitro-*o*-phthalic acid from the nitrophthalide (m. p. 141°) by oxidation. He found the best oxidizing agents to be a mixture of glacial acetic acid and chromic anhydride, or, better, dilute nitric acid in a sealed tube.

Oxidation by glacial acetic acid and chromic anhydride is far from satisfactory, and much the same may be said concerning the use of dilute nitric acid. The latter method is also open to the objection that it is not convenient for the preparation of large amounts of material.

Hoenig² further states that oxidation of the nitrophthalide by means of alkaline potassium permanganate gave no result. We have found, on the contrary, that this is much the best oxidizing agent for the purpose, 90 per cent. of the theoretical yield of 4,nitro-*o*-phthalic acid being thereby readily and rapidly obtained, the ease and rapidity of the method rendering it by far the best method of preparing the 4,nitro-*o*-phthalic acid pure and absolutely free from its isomer.

The oxidation is carried out as follows: *p*-nitrophthalide is dissolved in dilute alkali, the solution placed in a large evaporating dish on the water-bath, and potassium permanganate solution added gradually until the oxidation is completed. Excess of permanganate is then destroyed by the addition of a little alcohol, the manganese dioxide filtered off and the precipitate washed

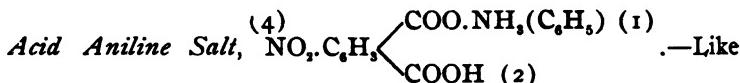
¹ *Ber. d. chem. Ges.*, 18, 3447 (1885).

² *Loc. cit.*

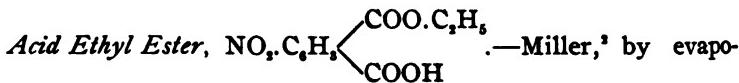
once or twice with hot water. The filtrate and washings are combined, concentrated to about 150 cc., acidified with hydrochloric acid, and repeatedly extracted with ether. The ether extracts are combined, dried with calcium chloride, and the ether evaporated, leaving the pure 4, nitro-*o*-phthalic acid as a pale yellow crystalline mass (m. p. 163°).

The 4, nitro acid loses water a few degrees above its melting-point, being thereby changed to the anhydride. The acid is easily soluble in water, methyl or ethyl alcohols, and acetone; moderately in ether or ethyl acetate; sparingly in cold isoamyl alcohol or glacial acetic acid, easily in hot; apparently insoluble in petroleum ether, benzine, chloroform, carbon tetrachloride, ethyl nitrate, carbon disulphide, benzene, and cold nitrobenzene; moderately soluble in hot nitrobenzene.

*Derivatives of 4, Nitro-*o*-phthalic Acid.*



the 3, nitro acid, the 4, nitro-*o*-phthalic acid appears incapable of forming neutral salts with the aromatic amines. As prepared by us, this acid aniline salt melts at 181°—182° with production of the anil. It has also been described by Graebe and Buenzod.¹ It seems probable that in these acid salts the para carboxyl carries the base.



rating an absolute alcohol solution of the 4, nitro-*o*-phthalic anhydride, reports the production of an acid ester different from the ordinary one (m. p. 127°—128°), but does not describe any of its properties. We have, therefore, repeated the experiment:

4, nitro-*o*-phthalic anhydride was dissolved in absolute alcohol in a flask fitted with a reflux condenser, the solution boiled for eight hours on the water-bath, and the alcohol then distilled off. A reddish brown oil remained. This oil dissolved, with effervescence, in sodium carbonate solution. The sodium carbonate solution was then extracted with ether, to remove any neutral ester which might have formed, the residual alkaline liquid acidified

¹ *Loc. cit.*

² *Ann. Chem. (Liebig)*, 208, 223 (1881).

with hydrochloric acid, and the turbid acid solution again subjected to extraction with ether. This ether extract was dried with calcium chloride and the ether evaporated, leaving a yellow oil, which, after standing about eight hours over sulphuric acid in vacuo, solidified to a pale yellow, amorphous mass, melting at 141° - 150° . Recrystallization failed to yield a substance with any sharper melting-point. The acid ethyl ester, produced by the action of dry hydrochloric acid gas upon the alcoholic solution of the 4,nitro acid, melts sharply at 127° - 128° . The acid ethyl ester described above appears, therefore, to be an isomer (although probably impure).

This result is rather at variance with the investigations of Wegscheider and Lipschitz¹ in preparing the methyl esters of 4,nitro-*o*-phthalic acid, as they obtained the same acid ester by the action of methyl alcohol upon the anhydride as by the action of hydrochloric acid gas upon the methyl alcohol solution of the free acid.

Anhydride, $\text{NO}_2\text{C}_6\text{H}_3(\text{CO})_2\text{O}$.—By heating the 4,nitro acid at

165° until no more water is evolved and then cooling, a sticky, yellow mass remains. Miller² heated this mass to 200° and sublimed the anhydride by passing a current of dry air through the melt. We have found it more convenient to dissolve this sticky mass in hot acetyl chloride and evaporate the solution to crystals. Pale yellow needles of the anhydride are thus obtained, melting sharply at 114° , which are easily soluble in acetyl chloride, hot glacial acetic acid or hot alcohol, and but sparingly in hot benzene.

Leupold³ prepared this anhydride by heating the acid in sealed tubes with acetyl chloride.

Imide, $\text{NO}_2\text{C}_6\text{H}_3(\text{CO})_2\text{NH}$, is prepared by the action of heat

upon the acid ammonium salt, in similar manner to the preparation of the imide of the 3,nitro acid. It crystallizes from a mixture of alcohol and acetone in pale yellowish brown flakes, melting at 197° . It is easily soluble in hot acetone, sparingly in hot alcohol or hot water.

¹ *Monatsh. Chem.*, 21, 787 (1900).

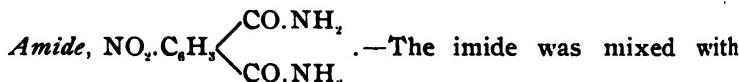
² *Ann. Chem. (Liebig)*, 208, 223 (1881).

³ *Inaug. Dissertation, Basle*, 1897.

- I. 0.1804 gram substance gave 24 cc. nitrogen at 23° and 755 mm.
 II. 0.1494 gram substance gave 19.9 cc. nitrogen at 22° and 756 mm.

	Calculated for $C_8H_7O_4N_2$.	Found.
	I.	II.
Nitrogen.....	14.62	14.96 15.00

By dissolving the imide in a mixture of alcohol and acetone and adding one molecule of alcoholic potassium hydroxide, the potassium salt of the imide separates as a white precipitate, slightly soluble in cold strong alcohol easily soluble in water.



strong ammonium hydroxide and dissolved by gentle warming. After standing for an hour at the temperature of the room, a heavy white crystalline precipitate appeared. This precipitate was filtered out, washed with a little cold water, and dried finally *in vacuo* over sulphuric acid. It then melted at 200° with evolution of ammonia, and when remelted, after solidifying, showed the melting-point of the imide (197°).

0.1430 gram substance gave 25.9 cc. nitrogen at 22.5° and 755 mm.	Calculated for $C_8H_7O_4N_2$.	Found.
Nitrogen.....	20.1	20.3

Amic Acid.—Attempts to prepare the aminic acid of the 4, nitro-*o*-phthalic acid by the same process that yielded the aminic acid of the 3, nitro-*o*-phthalic acid have so far been entirely unsatisfactory.

Ethylimide, $NO_2C_6H_5\begin{array}{c} CO \\ \diagup \\ \diagdown \\ CO \end{array} N.C_6H_5$, is prepared by the action of heat upon the acid ethylamine salt, or by heating the potassium salt of the imide in a sealed tube with ethyl iodide. Pale yellow scales (m. p. 111°-112°) are slightly soluble in hot water, readily in alcohol or ether.

0.1805 gram substance gave 20.6 cc. nitrogen at 23° and 758 mm.

	Calculated for $C_{10}H_8O_4N_2$.	Found
Nitrogen.....	12.7	12.83

Anil, $NO_2C_6H_5\begin{array}{c} CO \\ \diagup \\ \diagdown \\ CO \end{array} N.C_6H_5$, results when the acid aniline

salt is heated above its melting-point. It crystallizes from a mixture of alcohol and acetone in yellow needles, melting at

194°. It is moderately soluble in acetone, sparingly in alcohol. Graebe and Buentzod¹ give its melting-point as 192°.

Anilic Acid, $\text{NO}_2\text{C}_6\text{H}_4\text{COOH}$, is prepared by the action

of baryta water upon the anil. When the baryta solution is acidified with sulphuric acid the anilic acid precipitates with the barium sulphate, and must be extracted from it with cold alcohol. It forms pale yellow crystals, melting at 181° with formation of the anil. It is easily soluble in cold alcohol, nearly insoluble in ether, and apparently totally insoluble in cold water. Its solutions are acid to litmus but do not decompose carbonates.

0.1955 gram substance gave 17.2 cc. nitrogen at 25° and 761 mm.

Calculated for $\text{C}_{14}\text{H}_{10}\text{O}_6\text{N}_2$.

Found.

Nitrogen.....	9.8	9.83
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o-Nitranil, $\text{NO}_2\text{C}_6\text{H}_4\text{CO}\text{C}(\text{O})\text{N.C}_6\text{H}_4\text{NO}_2(o-)$, is prepared by

the action of heat upon the acid *o*-nitraniline salt. It crystallizes from nitrobenzene in pale yellow needles (m. p. 233°), difficultly soluble in acetone, very slightly in alcohol, and readily in hot nitrobenzene.

m-Nitranil is prepared in a similar manner from the acid *m*-nitraniline salt. It crystallizes from nitrobenzene in opaque yellow needles (m. p. 243°). It is sparingly soluble in alcohol or acetone, but readily in hot nitrobenzene.

p-Nitranil is prepared in a similar manner, crystallizes from nitrobenzene in small yellow crystals, melting at 251°–253°, difficultly soluble in acetone, apparently insoluble in alcohol, but easily soluble in hot nitrobenzene.

o-Tolil, $\text{NO}_2\text{C}_6\text{H}_4\text{CO}\text{C}(\text{O})\text{N.C}_6\text{H}_4\text{CH}_3(o-)$, is obtained by the

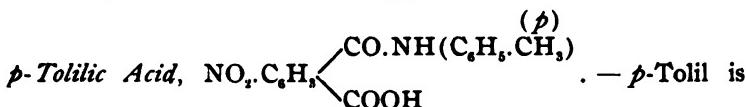
action of heat upon the acid *o*-toluidine salt, and forms a brownish crystalline powder (m. p. 160°). It is very slightly soluble in alcohol, moderately in acetone.

m-Tolil is prepared in a similar manner from the acid *m*-toluidine salt. Pale brownish crystals (from nitrobenzene, m. p. 197°) are practically insoluble in alcohol, difficultly soluble in acetone, easily in hot nitrobenzene.

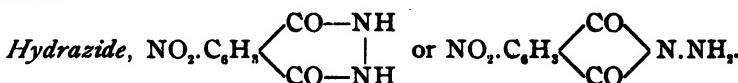
¹ Loc. cit.

p-Tolil is produced by heating together *p*-toluidine and 4,nitro-*o*-phthalic anhydride at 180°-190°. It crystallizes from a mixture of alcohol and acetone in yellow pearly flakes, melting at 165°, slightly soluble in alcohol, readily in acetone.

0.1935 gram substance gave	17.5 cc. nitrogen at 22.5° and 751 mm.	
	Calculated for C ₁₆ H ₁₀ O ₄ N ₂ .	Found.
Nitrogen.....	9.93	10.14



heated for fifteen minutes on the water-bath with baryta water, and the mixture then allowed to stand twenty-four hours at the room temperature. The flaky crystals of tolil are gradually replaced by long yellow needles of the barium salt of the tolilic acid. Upon the addition of sulphuric acid, the free tolilic acid precipitates with the barium sulphate and may be extracted from it by strong alcohol. On cold evaporation of the alcohol, the tolilic acid remains in white needles, melting at 172° (with formation of the tolil). The tolilic acid is insoluble in ether or cold water, does not decompose carbonates, but reacts acid to litmus.



—A solution of 4,nitro-*o*-phthalic anhydride was treated with one molecule of hydrazine hydrate (in 50 per cent. aqueous solution), and the mixture warmed for several hours. No precipitate formed, but, upon evaporation, a red oil remained, which changed to a yellowish brown precipitate when water was added. This precipitate was boiled down repeatedly with water, and finally washed with water, alcohol, and ether. In warm sodium carbonate solution it dissolved with effervescence, and reprecipitated in pale yellow flocks when the solution was acidified. Recrystallized from water, it forms a microcrystalline powder.

0.1503 gram substance gave	27.4 cc. nitrogen at 24° and 750 mm.	
	Calculated for C ₈ H ₆ O ₄ N ₂ .	Found.
Nitrogen.....	20.3	20.16

4,Nitro-*o*-phthalic acid was dissolved in water, one molecule of hydrazine hydrate added, the liquid evaporated to dryness, and the residue carefully heated. At 150° the mass began to soften

and evolve water, but the reaction did not appear completed until the temperature had reached about 250° . Even at this temperature the mass refused to melt, remaining hard and porous. It was purified by solution in sodium carbonate, reprecipitation, etc., as in the foregoing case, and yielded a similar product.

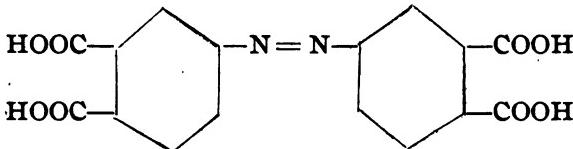
0.1733 gram substance gave 32 cc. nitrogen at 22° and 743 mm.

Calculated for $C_8H_5O_4N_2$.

Found.

Nitrogen.....	20.3	20.45
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The hydrazide forms small yellow crystals, slightly soluble in water or alcohol, difficultly soluble in glacial acetic acid. When heated to 270° it gives a white sublimate, then darkens at 280° , but does not melt even at 300° . Heated with acetic anhydride for several hours, no definite acetyl derivatives could be obtained.



4,4',AZOPHTHALIC ACID.

Preparation from 4, Nitro-o-phthalic Acid.—4, Nitro-o-phthalic acid was dissolved in dilute caustic soda, and the solution reduced by the gradual addition of 2 per cent. sodium amalgam. After the requisite amount of amalgam had been added, the mixture was heated for an hour upon the water-bath, the red alkaline solution decanted from the mercury, concentrated, and acidified with hydrochloric acid. A yellowish red precipitate appeared, which was filtered off, dried, and crystallized from water. It then formed a salmon-colored crystalline powder, moderately soluble in hot water, slightly in alcohol or glacial acetic acid, and insoluble in ether. It refused to melt at 360° . Its aqueous solution was acid to litmus and decomposed carbonates.

0.2046 gram substance gave 14 cc. nitrogen at 23° and 762 mm.

Calculated for $C_{16}H_{10}O_8N_2$.

Found.

Nitrogen.....	7.8	7.73
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The compound was unchanged by boiling with glacial acetic acid and sodium nitrite, showing the absence of hydrazo combinations.

The silver salt was prepared by adding a solution of argentic nitrate to the solution of the neutral ammonium salt. It separated as a red precipitate, insoluble in hot water, and when dried to

constant weight at 110° , appeared as a heavy red crystalline powder.

0.2039 gram substance yielded, upon ignition, 0.1085 gram silver.

	Calculated for $C_{10}H_8O_4N_2Ag_4$.	Found.
Silver.....	54.9	53.2

This low result is accounted for by the fact that the silver salt explodes when heated to a certain point, thus rendering the securing of accurate results a matter of considerable difficulty.

Preparation from Azophthalide.—An alkaline solution of 5,5'-azophthalide was oxidized by potassium permanganate in the manner already described for the conversion of nitrophthalide into 4,nitro-*o*-phthalic acid. By acidifying the filtrate from the manganese dioxide with hydrochloric acid, a reddish yellow precipitate separated, which was filtered off and dried. It then melted at 285° – 300° , with decomposition, and was crystalline in appearance.

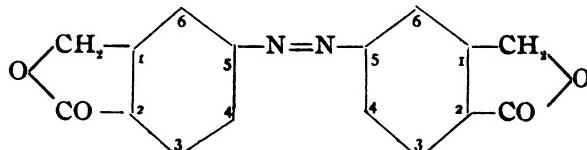
0.1946 gram substance gave 13 cc. nitrogen at 22° and 752 mm.

	Calculated for $C_{10}H_10O_4N_2$.	Found.
Nitrogen.....	7.8	7.8

The silver salt formed a heavy red crystalline powder, somewhat soluble in hot water, and exploded when heated.

It will be noted that the azophthalic acid obtained by this process melts, with decomposition, at a temperature somewhat below 300° , and gives a silver salt which is partly soluble in hot water, while that obtained by reduction of 4,nitrophthalic acid does not melt at 360° , and its silver salt appears to be insoluble in hot water. The cause of this difference has not as yet been determined. It will be made the subject of further investigation.

The corresponding 3,3',azophthalic acid has been prepared by Claus and May¹ by the reduction of the 3,nitro-*o*-phthalic acid with sodium amalgam, and forms golden yellow needles, decomposing at 220° – 250° .



¹ Ber. d. chem. Ges., 11, 762 (1878); 14, 1330 (1881).

5,5',Azophthalide.

This was obtained by the action of a 2 per cent. sodium amalgam upon the dilute alkaline solution of *p*-nitrophthalide. Hydrochloric acid is added to the resultant alkaline solution, and the red precipitate obtained is filtered off and dried. From dilute alcohol, it forms small red crystals, melting with decomposition at 260°–280°. It is sparingly soluble in hot water, moderately in hot alcohol or glacial acetic acid.

0.2000 gram substance gave 17.6 cc. nitrogen at 26° and 756 mm.

Nitrogen.....	Calculated for C ₁₆ H ₁₀ O ₄ N ₂ .	Found.
	9.5	9.6

This work is being continued and other papers upon the subject will be published.

ORGANIC LABORATORY, HAVEMEYER HALL,
COLUMBIA UNIVERSITY,
July 1, 1901.

ON THE EXISTENCE OF A NEW ELEMENT ASSOCIATED WITH THORIUM.¹

By CHARLES BASKERVILLE.

Received August 15, 1901.

ALMOST five years ago I attempted to separate thorium quantitatively from a neutral chloride solution by saturation with sulphur dioxide and boiling. As may be recalled, this was merely an application of the method formerly made known by me and used in the separation of zirconium² and titanium.³ The separation of thorium by this means was not quantitative. On resolution of the precipitated portion in hydrochloric acid and exact neutralization with ammonium hydroxide and treatment again with sulphur dioxide, almost complete precipitation resulted, showing that the initial partial precipitation was not altogether due to imperfect action of the precipitant or the solubility of the basic thorium sulphite⁴ in the neutral menstruum. This was verified by many repetitions of the process using thorium chloride solutions of different strengths and varying amounts of ammonium chloride.

¹ Presented at the Denver meeting of the American Chemical Society.

² *Chem. News*, **70**, 57 (1894); *This Journal*, **16**, 475 (1894).

³ *This Journal*, **16**, 437 (1894).

⁴ These basic sulphites are being investigated at present. It may be well to state that in addition to a flocculent basic sulphite there has been obtained a gelatinous compound, or hydrogele, similar in appearance to the zirconium sulphite described by Venable and Baskerville, *this Journal*, **17**, 448 (1895).

These solutions were first made upon fairly pure thorium salts prepared by me from oxides obtained from analyses of many monazite sands for the North Carolina Geological Survey.¹ As this conduct was unexpected and not in keeping with the observed reactions of the group, the experiments were repeated with thorium compounds obtained from different sources with like results. I was favored with several grams of thorium sulphate prepared by Professor Dunnington, of Virginia, from monazite sand found in Amelia County (Va.). Prof. Dennis, of Cornell, kindly gave me 3.5 grams thorium nitrate (99.6 per cent. pure). The hydroxide from which it had been prepared was separated by means of potassium hydronitrate.² I worked up about 5,000 liters of thorium sulphate solution obtained from Carolina monazite kindly collected by the late Mr. H. B. C. Nitze, assistant state geologist. The procedure followed need not be detailed here, as it will appear in a subsequent and more extended communication. Finally, Dr. Waldron Shapleigh generously gave me 2 kilograms of the purest thorium oxalate to be had at the Auer Welsbach works. My thanks are due these gentlemen for their kindness.³

The purest thorium compounds were repurified by the following procedure: The sulphate was taken up in cold water, treated with sodium sulphate and allowed to stand from twelve to twenty-four hours to insure separation of the remaining cerium salts, the percentage of which was quite small. The liquid was filtered

¹ Bulletin 9, "Monazite and Monazite Deposits in N. C.," 1895.

² This Journal, 18, 947 (1896).

³ While in the midst of repurifying the compounds from such varied sources and desiring to leave no stone unturned in the investigation, during the fall of last year I wrote Prof. Bohuslav Brauner, of Prague, of my observations and requested a small amount of the purified thorium compound used by him in his excellent work on the atomic weight of that element (*J. Chem. Soc., London (Trans.)*, 73, 951 (1898)). Very likely the letter went astray as I have received no reply. I was surprised, therefore, to observe in the proceedings of the London Chemical Society (April 10, 1901), an article by him on "Contributions to the Chemistry of Thorium," in which he gives good evidence of the complexity of thorium, dividing that element into Th_α and Th_β . Immediately at my first opportunity (April 23), at the spring meeting of the N. C. Section of the American Chemical Society, I made public mention of my work, which had been discussed often in private with others. Brauner's results were obtained by hydrolysis of the heptahydrated thorium tetrammonium oxalate. This communication contains in part the results of my experiments reported then and some observations made since. As soon as the unexpected properties were noted almost five years ago, I indicated the differences by terming one Th and the other $\text{Th}(\text{X})$. It is deemed well to make this explanation in presenting a preliminary paper on incomplete work, as it was done independently and the problem was attacked in a different way. Results have been obtained which corroborate Brauner's work. It may also be stated that large quantities of the materials are being worked up and the work will be pushed to a finality.

and the hydroxide precipitated in tall cylinders by a large excess of chemically pure sodium nitrite. This precipitate was washed by decantation from six to ten times, using 20 volumes (to 1 of precipitate) of distilled water each time. To remove the last of the sodium salts and other soluble impurities the precipitate was then dissolved in hydrochloric acid reprecipitated by slight excess of ammonium hydroxide and washed by decantation at least ten times, using 20 volumes of distilled water.

I. VARIATION IN THE SPECIFIC GRAVITY OF THE OXIDE.

The determination of the specific gravity of the oxides affords a rapid and excellent means of judging the rate of fractionation and in a measure the purity of the rare earths. This method has been especially urged independently by Muthmann and Bohm¹ as having time advantages over the necessarily long and often tedious equivalent determinations. Brauner also uses the method. The oxide obtained by prolonged ignition with the blast of the purified hydroxide obtained above had a specific gravity of 10.1 corrected to 4° C. Clarke,² in his "Constants of Nature," gives the following values :

Name and formula.	Sp. gr.	Authority.
Thorium dioxide, ThO ₂ .	9.402	Berzelius. ³
	9.21	Nordenskjöld and Chydenius. ⁴
	9.077	Chydenius. ⁵
	9.200	
	9.861	Nilson and Petterson. ⁶
	17° 10.2199	Nilson. ⁷
	10.2206 ⁸	
	15° 9.876 ⁹	Troost and Ouvrard. ¹⁰

About 10 grams of the purified hydroxide obtained above were again dissolved in hydrochloric acid, made up to about 300 cc., and exactly neutralized by dilute ammonium hydroxide. To insure neutrality, the ammonia was added until the slightest permanent precipitate remained after stirring the cold solution vigorously for five minutes. The precipitate was separated by

¹ Ber. d. chem. Ges., 33, No. 1; Chem. News, 81, 181.

² Smithsonian Institution, Part I, p. 48 (1868).

³ Pogg. Ann., 16, 385.

⁴ Jb. Chem., 13, 134.

⁵ Ibid., 16, 194.

⁶ Compt. rend., 91, 232.

⁷ Ber. d. chem. Ges., 15, 2336.

⁸ Reduced to 4° C., this value is 10.201.

⁹ Clarke gives a note stating that Nilson's determination is the only one of value.

¹⁰ Compt. rend., 102, 1422.

filtration and the solution saturated with freshly prepared and washed sulphur dioxide. Within a few minutes a flocculent basic sulphite began to separate. As the reaction continued in the cold the precipitate increased and then decreased somewhat. The solution was filtered cold and the filtrate boiled giving a second but much smaller precipitate similar to the first, showing that the precipitate is soluble to some extent in the cold sulphurous acid solution. The hot filtrate was then precipitated with a slight excess of ammonium hydroxide and filtered off. Portions of the sulphite and ammonia precipitates were removed from the funnels, care being taken that they were not contaminated with the ashless filter-paper, ignited in platinum crucibles with the blast and the specific gravity of the oxides determined.

Before treatment.	Sulphur dioxide precipitate.	Soluble portion precipitated by ammonia.
10.1	9.38	10.36 ¹

Twenty grams of Shapleigh's purest thorium oxalate were repurified according to the method given above. A saturated solution of chemically pure citric acid was prepared and the pure hydroxide added in excess; *i. e.*, until no more was dissolved cold when the stirring had continued (by means of a motor) for from twelve to fifteen hours (different experiments). In attempting to concentrate the filtered solution by heat a heavy white precipitate, resembling in a measure barium sulphate in appearance, came down. The utmost care was necessary in boiling the solution as the bumping was often quite violent. The precipitate redissolved when the solution was cooled. In evaporating the solution on the water-bath the precipitate appeared and was dissolved again on cooling.

A thorium citrate is described by Chydenius² but he did not investigate it further than to determine the percentage of oxide present. The investigation of this citrate, not previously noted, is well under way and will be published later as a separate paper. For our purposes here it suffices to state that the precipitate may best be obtained and separated by diluting the solution from five to ten times and holding it at or just below 100° C. This has been done by placing the large beaker (Jena glass) into a boiling water-bath for an hour. The precipitate settled well and the clear

¹ All determinations here and elsewhere in this paper were corrected to 4° C.

² Pogg. Ann., 119, 55 (1863); "Kemisk undersökning af Thorzord och Thorsalter" Helsingfors, 1861.

supernatant liquid was decanted; the precipitate was washed several times with boiling water by decantation, the settling occurring while the beaker was surrounded by boiling water. Finally the precipitate was thrown upon a large filter-paper and washed several times with boiling water, or until the wash-water was only faintly acid to litmus. The precipitate was carefully removed from the funnel, avoiding contamination with fibers of the filter-paper, and brought to a constant weight at 105°C . in an air-bath. Prepared thus the body is a beautiful white heavy amorphous powder and is an hydrated citrate of the real thorium.

Portions of this purified citrate made at different times were ignited in platinum crucibles with blast, and the specific gravity of the oxides determined.

Oxide taken. Gram.	Specific gravity, corrected to 4°C .
0.1989	9.234
0.6000	9.253
0.3830	9.210
0.4166	9.188 ¹

From these determinations it appears that Nordenskjöld and Chydenius very likely at one time had the nearly pure thorium compound. I am inclined to the opinion that the oxide obtained by me above is still not quite pure for reasons given below. (See also radio-active experiments.) One of the regrettable features of the paper is that I am unable yet to submit the results of the spectroscopic investigation of the material. Preliminary atomic weight determinations have been made from this oxide, however.

The filtrates (without the wash-water) obtained from the citrate mentioned above were concentrated in platinum on a water-bath. As the solution became concentrated a little more of the insoluble citrate separated out, but in one series of the experiments no effort was made to separate it, but the whole was carried down to a thick sirup and allowed to cool, when it became a mass of solid crystals, more or less opaque from the insoluble citrate bound up with the mass. Two grams of this material were ignited and the specific gravity of the oxide determined :

Oxide taken. Gram.	Specific gravity. ²
0.4000	10.50

¹ Citrate prepared from second heating of one of the solutions which was not completely precipitated at first.

² Mr. R. O. E. Davis, assistant in the laboratory, aided in some of the physical constant determinations. He is at present at work on the citrates and molybdates.

A larger quantity of the saturated citrate solution was prepraed dan most of the insoluble citrate removed according to the method given. About 2 liters of filtrate (wash-water not included) were concentrated to 400 cc. in platinum on the water-bath when a crystalline scum began to form. The dish was covered and allowed to stand over night. A few heavy crystals separated at the bottom. The thick sirup was drained from the crystals which, without crushing, were then washed three times with water, and dried at 120° C. On ignition, 31.61 per cent. of oxide was obtained. The specific gravity of the oxide was determined.

Oxide taken. Gram.	Specific gravity.
0.1789	8.77
0.2024	8.47

What this oxide is I am unable to say, unless it be the new body recently reported by Hofman and Prandtl¹ as a contamination of zirconium in euxenite. It constitutes only a very small percentage of the thorium and demands careful investigation, which I cannot at present undertake on account of the wealth of other material demanding more immediate attention. I should like to have the privilege of investigating it later, however.

When the sirup obtained above was further evaporated to about 300 cc., a white crystalline body separated and formed a thick coating on the bottom of the dish. The liquid was decanted, and the crystals washed until the water was only faintly acid, and dried at 120° C. The residue amounted to 16.20 per cent. after ignition, and had a specific gravity of 10.14, using 0.3820 gram of oxide.

On continued concentration small crops of crystals were obtained consisting primarily of citric acid with decreasing percentages of oxide. These salts have not yet been closely studied. When the sirup was brought to about 200 cc. it was diluted approximately to a liter and boiled. A small precipitate very similar to the first insoluble thorium citrate, yet different, was obtained. The oxide obtained when the material was ignited was exceedingly white.

Oxide taken. Gram.	Specific gravity.
0.1812	11.26

As the quantity of the material obtained was very small, too much weight should not be given to this value.

¹ *Ber. d. chem. Ges.*, 34, 1064 (1901).

Two portions of the filtrate from this precipitate were evaporated to dryness in a platinum dish, ignited, and the specific gravity of the residue determined:

	Oxide taken. Gram.	Specific gravity.
I.	0.3560	10.46
II.	0.8316	10.53

II was strongly ignited in a covered platinum crucible for three hours.

These determinations prove the presence of an oxide having an unusually high specific gravity, which cannot be accounted for except by the presence of either a new oxide of a known element having greater density than the usual non-volatile residue after ignition, or an unknown element. It is needless to say that the absence of such heavy substances as lead from the reagents was proved. From the variation in the values, assuming no error in manipulation, the oxide is not yet pure, but careful fractionation, using much greater quantities of the material, gives good promise.

II. EXPERIMENTS ON THE RADIO-ACTIVITY OF THE OXIDES.

In writing of the now well recognized Becquerel rays, M. and Mme. Curie¹ say that "the property of emitting rays * * * which act on photographic plates is a *specific property of uranium and thorium.*" Sir William Crookes² has practically proved that the radio-activity of uranium is due to a constant constituent, which can be partially fractioned out, Ur(X). In the same paper Dr. Crookes presents the results obtained in a few preliminary experiments he made to separate thorium compounds into an active and inactive body.³ His experiments in fractioning thorium sulphate gave negative results. However when he obtained six fractions by crystallizing the nitrate, "the oxide from the first end crystals gave a feeble action, while the other end gave an impression about three times as intense. This points to the possibility of separating from thorium its radio-active substance" (p. 421). My own experiments are in exact accord with the above. The oxide (sp. gr. 9.25) obtained from the insoluble citrate affects the sensitive plate in the dark after an exposure of seventy-two hours but slightly, while the oxides of higher specific gravity are quite active. A number of plates have been exposed, using oxides

¹ *Compt. rend.*, 127, 175; *Chem. News*, 78, 49 (1898).

² *Proc. Roy. Soc.*, 66, 409.

³ *Loc. cit.*

obtained through the research, monazite sand from which the thorium salts were prepared, uranium nitrate, acetate, uraninite, and blanks for comparison. The radio-activity increased with the increase in specific gravity. For reasons given below I am of the opinion that the 9.25 thorium oxide is not quite pure, that is, free from traces of the higher oxide, hence its faint activity. (See above. Method of application is outlined below.)

I am not yet ready to assert that the new substance obtained is not the third radio-active body reported by Debierne in pitch-blende,¹ actinium, which, he states, belongs to the iron group. From Madame Curie's statement, Debierne supposes that the radio-active property observed in thorium compounds does not belong to this element, but is due to a foreign material, hence actinium (?). From Rutherford's experiments on induced radio-activity, one is loath to accept the radio-activity of unprotected bodies as sufficient evidence of their sameness. I have not so far had time to apply the radiant matter test, but amassing chemical evidence so far obtained points to the presence of a hitherto unrecognized body.

An account of the method used in these preliminary experiments on the radio-activity of thorium and its constituents may be of interest. The plan was essentially the same followed by Dr. Crookes,² differing somewhat in details. Placing small circular pill boxes containing the materials directly on the same sensitive plates was not satisfactory on account of the excessive radiation from the concentrated active body in all directions. Black glazed paper, the size of the plate, was punctured with circular holes about 1.5 cm. in diameter and placed dark side up on the plate. A sheet of silver-free lead, about 0.5 mm. thick, was similarly cut and placed on the paper, which served to protect the plate. The material was placed in quantities varying from 0.25 to 1 gram in small exhibition glass tubes 1 cm. in diameter and 5 cm. tall. These cells were closed by sealing thin circular microscope slide covers to the flange with Canada balsam. After air-drying, the cells were inverted and the sealed end placed neatly over the circular openings in the lead and paper, thus exposing portions of the plate to the radiant action downward through a thin medium of glass and air, as the cells were not in contact.

¹ *Compt. rend.*, October 10, 1890, and April 2, 1900; *Chem. News*, 81, 169.

² *Loc. cit.*

with the sensitive surface nearest the tubes being held up by the flange, which projected beyond the circular opening. To eliminate lateral radiant action, each cell was then surrounded by a cylinder of lead, which was filed to fit snugly upon the sheet lead below. These cylinders were about 2.5 cm. in diameter, inside, and 5.25 cm. high. Such a battery, having from two to eight cells differently charged, was placed in a box, closed, covered with black glazed paper, several thicknesses of cloth and locked in a dark room for various lengths of time, 24 to 145 hours. The plates were afterwards developed.

III. DETERMINATION OF THE ATOMIC WEIGHT OF THORIUM.

As this is a preliminary paper, a detailed discussion of the various atomic weights accorded thorium by the several workers is beyond its scope and will be reserved for a subsequent communication. Suffice it to say the compounds made use of, as reported by Clarke,¹ *viz.*, the sulphate, oxalate, acetate, and formate, offer little promise of either concordant or satisfactory results. Brauner and Povlicek² have recently called attention to a serious source of error in using the anhydrous sulphate. The careful work of Brauner on the heptahydrated thorium tetrammonium oxalate³ gives good results for that substance, but in atomic weight work it is desirable to have as few factors as possible for consideration. It is a matter for surprise that none of the halogen compounds have ever been used. The tetrachloride was selected for this preliminary work. It may be that the bromide will yield even better results.

Preparation of Thorium Tetrachloride.—Thorium dioxide was prepared from the purest insoluble citrate by intense ignition, ground to an impalpable powder in an agate mortar and an intimate mixture made with a thick paste composed of corn starch and pure sucrose sirup. Balls, 5–8 mm. in diameter, were made from this, dried and baked at 140°–150° C. in a platinum milk pan until thoroughly browned. They were then heated in a closed platinum crucible with a Bunsen burner until thoroughly carbonized. About a dozen of these black pellets were placed into a perfectly clean dry combustion tube. Freshly prepared, pure dry chlorine was passed through the tube, that portion immediately

¹ Smithsonian Institution, "Constants of Nature," V, revised, 1897, p. 204.

² Proc. Chem. Soc. (Lond.), 17, 63 (1901).

³ Chem. Soc. Trans. (Lond.), 78, 951 (1898).

surrounding the balls being heated to dull redness. At first a white vapor formed; some settled on the tube quite a distance from the heat and some was swept into the lime absorption tower by the chlorine. In Chydenius' paper¹ it appears that Berzelius observed this "weisser dampf" and he states that it is not finely divided thorium chloride. This is the impurity which was noted above. Then beautiful fern-like crystals, only slightly volatile, began to form immediately over and on the balls. These crystals are the purest compound of thorium ever prepared in this laboratory.² After two hours the heat was removed and the tube allowed to cool in a current of chlorine, which was subsequently removed by pure dry air free from carbon dioxide.

These crystals absorbed water and were quite soluble. The white volatile vapor mentioned was even more deliquescent. The fernoid crystals were dissolved in water, the solution made up to 100 cc. in a standard flask, and aliquot portions measured out by means of a calibrated standard burette, whose outlet was so constricted as to deliver 0.01 cc. by drops.

Those portions taken for the determination of thorium were measured directly into weighed platinum crucibles, which were placed into perforations of a porcelain plate over a water-bath, and evaporated to dryness. The gelatinous oxychloride was gently heated first over a Bunsen burner and then ignited to a constant weight over the blast-lamp. A beautiful white glistening residue of thorium dioxide was obtained.

For the determination of chlorine, measured quantities were taken, diluted to 75 cc., and acidified with 1 to 2 drops pure nitric acid. Just below the boiling-point the chlorine was precipitated with a weighed quantity of silver nitrate prepared according to Stas. The precipitate was caught in a weighed Gooch crucible, the suction flask being placed in an asphalted box. The crucible and silver chloride were then dried in a dark air-bath at 140°-150° C. to a constant weight. The acid-washed asbestos from which the felt was made was previously digested in boiling hydrochloric acid, then water, then hot nitric acid, and finally washed with boiling water until not the faintest evidence of the presence of halogens was obtained.

¹ *Loc. cit.*

² I was assisted in the preparation of the tetrachloride and dry ether by Dr. A. S. Wheeler, associate professor, to whom I wish to express thanks.

The following are the results obtained :

	Taken.	Thorium dioxide found.	Per 100 cc.
A. {	25 cc.	0.0903	0.3612
	10 cc.	0.0812	0.2007
B. {	15 cc.	0.0542	0.36133
	15 cc.	0.1220	0.20105

Calculations :

$$\begin{aligned} A. \frac{XO_2}{Cl_4} &= \frac{0.3612}{0.2007} \quad \therefore X = 223.2 \\ B. \frac{XO_2}{Cl_4} &= \frac{0.36133}{0.201056} \quad \therefore X = 223.3 \end{aligned} \quad \left. \right\} \text{Atomic weight of thorium.}$$

It is very interesting here to note that both Hermann's¹ and Delafontaine's² results obtained from $2\text{ThSO}_4 \cdot 9\text{H}_2\text{O}$ and corrected by the observations of Hillebrand³ to $\text{ThSO}_4 \cdot 4\text{H}_2\text{O}$ give 223.06 ± 3426 . On account of the doubt as to the composition of the sulphate and the wide divergence in the value obtained (223.23) from the accepted atomic weight of thorium, Clarke correctly threw it out of consideration. From the preliminary values obtained above, which were not reduced to a vacuum, the results assume importance.

As the tetrachloride is so readily decomposed by water and a direct comparison between a known amount of the tetrachloride and the oxide obtained therefrom is desirable, a complete analysis of the body was made.

Preparation of Pure Anhydrous Ether.—Ether, which had stood over calcium chloride for a year, was decanted over fresh fused calcium chloride and allowed to remain a week. It was then distilled and placed over freshly cut sodium and allowed to stand four days. It was again distilled and placed over fresh sodium and left three days until no more bubbles of hydrogen escaped. This process was repeated until fresh sheets of sodium showed no tarnishing and no hydrogen bubbles were observable. It was finally distilled. In all these operations special precautions were taken to prevent the absorption of a trace of moisture.

More tetrachloride was prepared and that part of the tube on each side and just above the pellets was placed in a perfectly dry Soxhlet apparatus. At the upper end of the reflux condenser

¹ "Constants of Nature," Clarke, Part 5, revised, 1897, p. 204.

² Arch. sci. phys. et nat., (2), 18, 343.

³ Bulletin 90, U. S. Geological Survey, p. 29.

was attached a calcium chloride tube. After the apparatus was in place it was learned that the ground-glass connection of the condenser was not air-tight. A selected velvet cork was substituted. When the extraction had continued about six hours, it was discovered that an overlooked small defect of the cork had permitted the gradual introduction of about a drop of water, which came from the sweating of the condenser overhead. As this vitiated the experiment, the ether was evaporated and the whole dissolved in water. During the evaporation a small amount of hydrochloric acid was detected in the vapor. For that reason the experiment must be discarded, but the results are given :

C. { Thorium dioxide found	0.1020
Chlorine found.....	0.05636

whence

$$\frac{\text{XO}_2}{\text{Cl}_4} = \frac{0.102}{0.05636} \dots 234.65 = \text{atomic weight.}^1$$

The pellets, which were covered with excrescences of crystals of the tetrachloride, were repeatedly shaken in a small Erlenmeyer flask with about 10 cc. of pure dry ether. The ether was filtered directly into a weighed platinum crucible, which was placed in a vacuum desiccator, in the bottom of which was pure concentrated sulphuric acid and above chipped paraffin. The tetrachloride appears to be soluble in about 1000 parts of dry ether. Proper precautions were taken to dry the air used to relieve the vacuum of the desiccator and prevent back rush of moist air from the pump. The crucible was dried at 105° C. for half an hour in an air-bath already heated and weighed. The finely crystallized tetrachloride was dissolved in 2 cc. of pure distilled water to decompose the chloride and form the oxychloride, evaporated to dryness, ignited, and weighed. The following results were obtained :

Tetrachloride used..... 0.0822 gram.

Dioxide found..... 0.0574 gram.

$$\text{Hence } \frac{\text{XO}_2}{\text{XCl}_4} = \frac{0.0574}{0.0822} \therefore 222.13 = \text{atomic weight.}$$

In all calculations the following values were used : O = 16, Cl = 35.45, and Ag = 107.93.

Another ether extract was made as above, weighed and dissolved in water and the chlorine determined by titration with a standard silver nitrate solution, using potassium chromate as indicator,—method of Pelouze. Tetrachloride used, 0.01 gram;

¹ Higher chlorine value decreases the atomic weight of thorium.

cubic centimeters of silver nitrate required, 3.9, each cubic centimeter being equivalent to 0.001 gram chlorine; hence 0.0039 gram chlorine or 39 per cent. The percentage of the oxide obtained from the chloride, 69.83.

	Calculating for ThCl ₄ , using 222.	using 223.3.	Found.
Th.....	61.03	61.18	
or,			
ThO ₂	69.83	70.17	69.83
Cl ₄	38.97	38.84	59.00

These discrepancies do not deserve discussion as the data are far too few for ascribing the proper atomic weight to thorium. The last analysis is important, however, as we have secured a substance of known composition, which may be prepared pure and which lends itself for atomic weight determinations, as the dual constituents, thorium and chlorine, can be determined with accuracy. The figures hold interest however, as it may be asserted that the real mass equivalent of thorium is much below that hitherto ascribed to it. It is of greater interest to attribute the old values to a constant unknown impurity in practically all the materials used. This constituent must be an element of much higher atomic weight.

With this evidence of the complexity of thorium the problem now engrossing my personal attention is the separation of the compounds of this element, the proof of their purity and determination of the physical constants and chemical properties. From insufficient data already obtained, in case the element be tetravalent, it appears that the atomic weight lies between 260 and 280. On account of the extensive occurrence, in this state (North Carolina), of the monazite sands from which the original material was obtained, if the investigation give a successful issue, I should like to have the element known as *Carolinium*, with the symbol *Cn*.

As this is a preliminary paper only, it may not be out of place to state the lines of research bearing immediately upon the subject that are already under way in this laboratory.

1. The preparation of an adequate quantity of perfectly pure thorium compounds with which to continue the study of the radio-activity, the spectrum, and to obtain sufficient tetrahalides

for the determination of the true atomic weight of that element, which is assuredly different from the number usually accorded it and dependent at present upon evidence not wholly satisfactory.

2. An investigation of several of the old thorium compounds, like the hydrated sulphates, citrates, etc., and determination of their composition.

3. An investigation of the volatile chloride obtained in the preparation of the thorium tetrachloride.

UNIVERSITY OF NORTH CAROLINA,
June 1, 1901.

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CONTRIBUTIONS TO THE STUDY OF RUTHENIUM, IV.¹

THE CHLORIDES.

BY JAS. LEWIS HOWE.

Received August 29, 1901.

In his early work upon ruthenium, Claus described two classes of chlorides, $\text{Ru}^{\text{II}}\text{Cl}_3 \cdot 2\text{XCl}$, and $\text{Ru}^{\text{IV}}\text{Cl}_4 \cdot 2\text{XCl}$, corresponding to two of the general types among the metals of the platinum group; the former made by the action of hydrochloric acid upon any of the soluble oxides or hydrated oxides, the latter, generally at least, by oxidation with nitric acid. The trichloride is formed also when chlorine acts directly upon the metal, especially in the presence of alkaline chlorides.

In addition to these chlorides, Claus called attention to the fact that by the action of hydrogen sulphide, the deep red-brown solution of ruthenium trichloride becomes dark azure-blue, probably owing to reduction to a bichloride, $\text{Ru}^{\text{II}}\text{Cl}_2$. No further advance was made on the chlorides till A. Joly² showed that the chloride obtained by oxidation with nitric acid is not as Claus had supposed the tetrachloride, but a nitrosochloride, RuCl_4NO . More recently U. Antony³ has shown that by adding potassium

¹ Read in abstract at Denver meeting of the American Chemical Society.

² *Compt. rend.*, 107, 994 (1888); 108, 854 (1889).

³ *Gazz. chim. ital.*, 29, 1 (1889).

ruthenate, K_2RuO_4 , to hydrochloric acid, the true tetrachloride, $Ru^{IV}Cl_4 \cdot 2KCl$, is really formed, and it appears quite possible that Claus may have had this salt in hand, and in one case have analyzed it. He did not at all events distinguish it from the nitrosochloride. Joly¹ also studied the azure-blue solution of the reduced chloride and concluded that it contains an oxychloride, $RuCl_3 \cdot OH$.

The nitrosochloride series of salts has been quite fully worked out by Joly,² Brizard,³ and the author.⁴ The present paper extends the trichloride series of Claus and the tetrachloride series of Antony, to some of the cesium and rubidium members, and presents two members of a new series, $RuO_2Cl_4 \cdot 2XCl$, an oxychloride intermediate between the tetroxide and tetrachloride. A few notes are appended on the blue solution.

Ruthenium Tetrachloride.—When hydrochloric acid, or free or nascent chlorine, acts upon ruthenium compounds, in almost every case, the trichloride is the resultant product. Joly, as well as the author, tried in vain, by various methods of chlorination, to form the tetrachloride. Apparently $RuCl_4$ will not take up another atom of chlorine. Antony first wittingly prepared the chloride, using potassium chlorate to oxidize the ruthenium to ruthenate, thus insuring the absence of a nitrate and hence of nitrosochloride formation. The solution of the ruthenate was then added to dilute hydrochloric acid. On the other hand, when the acid is added to the ruthenate, even at a temperature below zero, and the solution concentrated in the cold, the trichloride is the only product I have been able to obtain. The study of the conditions of formation of the tetrachloride are much enhanced in difficulty by the close resemblance of its solutions to those of the trichloride. I have as yet noted but a single analytical reaction in which the two compounds differ sufficiently to be readily distinguished, and this reaction demands the dry salt free from acid and in a fairly pure state; nor is it easy, even by the microscope, to distinguish the presence of the tetrachloride in a mixture.

The starting point of the work of the present paper was generally ruthenium tetroxide, RuO_4 , distilled from the alkaline ruthenate solution by a current of chlorine. In the earlier part of

¹ *Compt. rend.*, 114, 291 (1892).

² *Loc. cit.*

³ *Bul. Soc. Chim.* [3] 13, 1092 (1895); *Compt. rend.*, 122, 730 (1896).

⁴ This Journal, 16, 388 (1894).

my work, the ruthenate was formed by fusing metallic ruthenium, or ruthenium residues of any kind (which must be free from osmium) with caustic potash and saltpeter, in a silver dish. The introduction of sodium peroxide into the laboratory has occasioned much economy of time and trouble in this operation. The ruthenium, in any finely divided form, is slightly mixed in a nickel dish with three or four times its volume of sodium peroxide and warmed with occasional stirring till it becomes nearly but not quite completely fused. The conversion into sodium ruthenate is rapid and generally complete, and the melt is readily soluble in a small quantity of water. To avoid undue heating, it is well to rest the nickel dish in a beaker full of cold water, or on a piece of ice, while dissolving the melt. The strong solution of the ruthenate is poured into a small tubulated retort, and through it is passed a fairly rapid current of chlorine. As the solution becomes saturated, the ruthenium tetroxide begins to pass off as a golden yellow vapor, and may be completely removed from the solution by gently warming and finally bringing to a boil. When it is desired merely to obtain a pure ruthenium, the tetroxide may be led directly into dilute alcoholic potash, but when the pure tetroxide is desired, an adapter is arranged leading into a large, stoppered test-tube, and from this any uncondensed tetroxide together with the chlorine is led into an aqueous solution of potash. Beyond the potash bottle may be placed a bottle of alcoholic potash, which will effectually retain every trace of ruthenium. Before the introduction of the aqueous potash bottle, it was found that the vapors of alcohol diffused slightly into the tetroxide tube, causing decomposition. In one instance owing to the stopping of the chlorine current a little of the alcoholic potash was drawn over into the tube, which then contained perhaps 3 or 4 grams of the tetroxide. A very violent explosion occurred which shattered the apparatus, and filled the room with dense black smoke. This ruthenium soot, evidently an oxide, differs from any described anhydrous oxide, in being very soluble in dilute hydrochloric acid. The trichloride is formed.

If the absence of osmium be assured, this method of preparing the tetroxide or of purifying ruthenium is very satisfactory, being fairly expeditious and without danger. The fumes of ruthenium tetroxide, though somewhat suffocating, appear to have the

irritating and poisonous qualities of the osmium tetroxide to a very slight degree if at all.

When ruthenium tetroxide is treated with hydrochloric acid in the cold, it is slightly soluble to a light reddish yellow solution. On standing, or on warming, the solution becomes dark red and chlorine is evolved. The rapidity of this change is proportional to the strength of the acid, and to the temperature. In five times normal acid, at ordinary temperature, some unchanged RuO₄ is present in the solution after standing several days. The primary product obtained on treating the dark red solution with an alkaline chloride is the trichloride, of formula Ru^{III}Cl₂XCl generally at least with one molecule of water, and until recently no other compounds have been recognized.

If, however, ruthenium tetroxide is covered with water, in which it is but slightly soluble, a strong solution of cesium (or rubidium) chloride added, and the whole acidified with a small amount of hydrochloric acid, the tetroxide is gradually converted into the double salt of the oxychlororuthenate to be described in the next paragraph. This salt on boiling with concentrated hydrochloric acid is converted into the double salt of ruthenium tetrachloride, but some of the trichloride seems to be formed at the same time. Many efforts were made to obtain the tetrachloride directly from the tetroxide, but the exact conditions of the reaction were not found; the tetrachloride, however, not seldom appeared in the products. The best specimen obtained (analysis 3) was the second crop of crystals from evaporating the filtrate from the precipitation by alcohol of the reaction products of the tetroxide, cesium chloride, and concentrated acid. The previous crop had consisted of a mixture of the tetrachloride, and a rose salt to be mentioned later. Cesium and rubidium chlororuthenates, Cs₂Ru^{IV}Cl₆ and Rb₂Ru^{IV}Cl₆, when well crystallized, consist of black, almost opaque, regular octahedra, resembling the corresponding salt of the other platinum metals; when precipitated from solutions by alcohol, they are buff powders, hardly distinguishable as crystalline. They are almost insoluble in cold water, barely tinting the water brown; on heating, the solution becomes darker and slightly purplish, the salt being decomposed. If now a drop of concentrated hydrochloric acid is added, a deep purple color is noticeable in the brown solution, but it soon disappears, leaving the solution brownish. This reaction, which is very sat-

isfactory if the salt is quite pure, is the only one yet found which differentiates clearly the tetrachloride from the trichloride. The tetrachloride is less soluble in concentrated hydrochloric acid than the trichloride; is fairly soluble in hot dilute hydrochloric acid. The solution in hydrochloric acid resembles that of the trichloride, save for a slight cast of pink to the deep red concentrated solutions, and a pure yellow in dilute solutions, as against the reddish cast to the yellow of the trichloride.

The alkalies give a dull greenish blue precipitate (or color only with ammonia); with all other reagents tested, the reactions in no wise differed from those of the salts of ruthenium trichloride. When acidified with hydrochloric acid and boiled in dilute solution, especially with alcohol, the solution becomes rose, and on slow evaporation the rose prisms described later are found together with the octahedra of the unchanged tetrachloride.

Cesium and Rubidium Oxychlororuthenate, $\text{Cs}_2\text{RuO}_2\text{Cl}_4$ and $\text{Rb}_2\text{RuO}_2\text{Cl}_4$ ($2\text{CsCl}, \text{RuO}_2\text{Cl}_4$, and $2\text{RbCl}, \text{RuO}_2\text{Cl}_4$).—These salts are slowly formed by the action of a solution containing little hydrochloric acid and much alkaline chloride, on excess of ruthenium tetroxide, in the cold. Owing to the volatility of the tetroxide and its instability, especially in the presence of any organic vapors, the best method of preparing the salt was found to be as follows: Two or three grams of ruthenium tetroxide (more or less water is in the distillate used) were poured into a glass weighing-tube of 3 cm. diameter. A few cubic centimeters of a quite concentrated solution of cesium (or rubidium) chloride were added and a few drops of concentrated hydrochloric acid. The tube is then stoppered and shaken from time to time. The stopper must be occasionally removed to permit the escape of the chlorine generated. In the course of twenty-four hours, a considerable crop of the crystals of the salt may be removed, dried on a tile, and after the volatilization of the ruthenium tetroxide which will be present, the salt may be washed by a trace of hydrochloric acid. Successive crops may be obtained. These salts consist of dark purple isometric crystals, showing the octahedron, cube, and rhombic dodecahedron. They are quite soluble in cold hydrochloric acid to rose solution, yellow on dilution; from cold solution, the salt crystallizes out unchanged, even in the presence of alcohol.

On heating with hydrochloric acid, chlorine is evolved and the

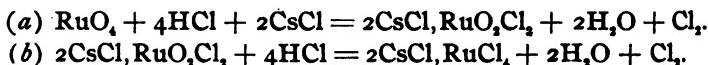
corresponding salt of ruthenium tetrachloride crystallizes out.

The characteristic reaction of the oxychlororuthenate is its instant decomposition by water. When even a very small crystal is let fall into a drop of water on a watch-glass, it at once dissolves and decomposes, rendering the whole drop a black liquid. At the same time there is noticeable a marked odor of ruthenium tetroxide. The salt is also decomposed by sulphuric and nitric acids with the evolution of the same odor.

These two salts belong to a type with very few representatives. Péligot by the action of hydrochloric acid on potassium uranate obtained $2\text{KCl}, \text{UO}_2\text{Cl}_2, 2\text{H}_2\text{O}$, and Sendtner prepared the corresponding bromide.

By the action of hydrofluoric acid on potassium tungstate, Berzelius obtained $2\text{KF}, \text{WO}_3\text{F}_2, \text{H}_2\text{O}$ and two or three other analogous tungstates. The chlorotungstate WO_3Cl_2 , like the corresponding MoO_3Cl_2 and CrO_3Cl_2 , exhibits no tendency to form salts. Piccini's ammonium fluotitanate, $3\text{NH}_4\text{F}, \text{TiO}_2\text{F}_2$, seems rather of the nature of a peroxide.

The uniform nature of the oxychlororuthenate was evident under the microscope, before and after recrystallization. The absence of water or of hydroxyl groups in the salt was shown by heating in oxygen stream in a tube guarded at either end with a phosphorus pentoxide tube (see Analysis 9). This shuts out the possibility of the salt being $\text{Ru}(\text{OH})_2\text{Cl}_4$. The formation of the salt and its decomposition with hydrochloric acid are shown by the formulas :



The odor of ruthenium tetroxide, when the salt is decomposed by water or other acids than hydrochloric, may be the odor of ozone, the formation of which would be readily explicable. When ruthenium tetroxide comes in contact with any organic substance it is instantly decomposed, and it may well be that the oxide is decomposed before stimulating the olfactory nerves, and the odor recognized is that of ozone, formed by the decomposition of the oxide. At least the two odors resemble each other very closely.

Ruthenium Trichloride Salts.—The salts of the lighter alkali metals have been fully described by Claus and Joly. Cesium and rubidium chlorides show the familiar tendency to form complex

salts with ruthenium trichloride, according to the conditions of experiment. The normal salts are $Cs_2RuCl_6 \cdot H_2O$ and $Rb_2RuCl_6 \cdot H_2O$, the presence of the water of crystallization being confirmed by Analyses 13 and 17. The water is slowly driven off by heat and at 250° one atom of chlorine is very slowly lost.

Indications of more complex salts were obtained and several analyses of these are appended. In most of these cases there is no assurance that the salt, always difficult to dry, was pure or uniform (except 21), but the fact that salts of approximately the same composition were obtained from different sources, points to the probability that they are definite compounds.

One salt, however, of this class is characterized by forming uniform, transparent, rose prisms, with extinction parallel to the prism. These are deposited from the rose solution obtained when a slightly acid solution of the tetrachloride is heated with considerable excess of water and alcohol. It is also deposited from the filtrate after the electrolytic reduction of the trichloride. It is also probably formed in dilute solutions of the trichloride, but it has not been analyzed, nor positively identified from this source. It is not very soluble in hydrochloric acid, and is very slightly soluble in water. It can be crystallized apparently unchanged from hydrochloric acid, but on evaporating to dryness in hydrochloric acid solution, some tetrachloride is formed. The composition of these rose prisms is $Cs_2RuCl_6 \cdot H_2O$, the same as that of the normal cesium salt of the trichloride, but they are very distinct from that salt, and should probably be looked upon as an *aqua* salt, $2CsCl_2 \cdot Ru(OH_2)Cl_3$, corresponding to the tetrachloride, $2CsCl_2 \cdot RuCl_4$.

Ruthenium Dichloride (?).—Forty years before the discovery of ruthenium by Claus, Vanquelin had noticed the azure-blue color produced by the action of zinc upon certain solutions, a reaction which he attributed to osmium. One of the most characteristic reactions of trivalent ruthenium is this blue color formed by the action of hydrogen sulphide. Since it is produced by the action of reducing agents upon the solution of ruthenium trichloride, Claus attributed it to the formation of a bichloride, but he did not separate the salt. When a mixture of chlorine and carbon monoxide is passed over finely divided ruthenium at a comparatively low temperature, a very voluminous powder is obtained which contains anhydrous trichloride, as shown by Joly. This

is insoluble in water, acids, and strong alcohol, but is freely soluble in dilute alcohol, to the same dark azure-blue solution. On distilling the solution in vacuum, Joly obtained what he considered to be an oxychloride, and he looked upon the blue solution as Ru(OH)Cl_3 . Inasmuch as in the solution of this variety of the trichloride, aldehyde is formed, and since the blue color is produced in every case by a reducing action, it seems to me probable, that a true bichloride is present. In spite of much effort, I have not succeeded in preparing a pure salt from the blue solution, but several that have been prepared point to a compound of the formula $3\text{CsCl}_2\text{RuCl}_3 \cdot 2\text{H}_2\text{O}$. These were formed by reducing a solution of ruthenium trichloride in an electrolytic cell, and immediately adding a solution of cesium or rubidium chloride. The fine precipitate varies from dark greenish blue to olive-green, oxidizes with great rapidity, and is very difficult to filter and wash, even under suction. Analyses of a number of the precipitates are given, two of which, 24 and 25, point to the above formula. In the others the amount of chlorine is too large in proportion to the ruthenium for RuCl_3 , though in every case less than is required for RuCl_3 . The addition of cesium chloride to the blue alcoholic solution of the anhydrous trichloride causes a precipitate much resembling that from the solution obtained by electrolytic reduction, but it has not yet been found possible to filter it off and wash it. The investigations upon the blue solution are still being carried on.

Another investigation now in progress may also be mentioned in this connection. An attempt was made to reduce the trichloride of ruthenium by stannous chloride. If the salt is not completely in solution a fugitive greenish blue solution is produced, but in general the dark yellowish red solution of the trichloride becomes much lighter, and if dilute, is almost completely decolorized. On adding water to this solution a yellow flocculent precipitate is formed, which contains all the ruthenium which was in the solution. This precipitate is insoluble in hot water, but easily soluble in hydrochloric acid, from which it is again precipitated on dilution. From the hydrochloric acid solutions are obtained two crystalline salts: one consists of white to pale yellow octahedra of cesium (or rubidium) chlorostannate, thus showing an oxidation of the tin; the other crystals are brilliant red (apparently) octahedra. These seem to be perfectly uniform

and analysis shows them to contain both tin and ruthenium.

For the material used in my work, I am indebted to Johnson, Matthey and Co., of London, for crude ruthenium; to Baker & Co., of Newark, N. J., for the use of several ounces of iridium; and to the Imperial Academy of Sciences, through its president and Professor N. N. Beketoff, director of its laboratory, for a considerable quantity of ruthenium.

ANALYTICAL WORK.

The analysis of most of the salts described in this paper was carried out by heating 0.2 to 0.35 gram of the salt contained in a platinum or at times in a porcelain boat, in a combustion tube in a current of hydrogen. The hydrochloric acid evolved was collected in a solution of silver nitrate, guarded by a second silver nitrate solution, to prove complete absorption of the gas. This gave the chlorine freed from the ruthenium by heat. The residue, consisting of ruthenium and alkali chloride, was extracted with hot water, followed by dilute acid. The alkali chloride was then determined, either by evaporation or by precipitation of the chlorine. The ruthenium was heated in a hydrogen stream before weighing; occasionally the ruthenium, on being brought to the air, glowed, and was slightly oxidized, giving results a little too high.

For the direct determination of water, or hydroxyl groups, the salt was heated in oxygen in a porcelain boat, and several coils of silver foil kept in front of the boat. The rear end of the combustion tube was guarded by a phosphorus pentoxide tube, and the gas from the tube passed through a weighed phosphorus pentoxide tube. The chlorine given off in the oxygen stream was almost completely held by the first silver coil. After heating in oxygen, the phosphorus pentoxide tube was removed, silver nitrate solution substituted, and the analysis continued in a hydrogen stream in the usual way. The only defect of this method is that, even at the low heat used, a small quantity of ruthenium is volatilized in the oxygen; hence, where this method was used the ruthenium is a little low.

Cesium Chlor Ruthenate, Cs_2RuCl_6 .—Dark brown to black powder; under the microscope black octahedra; larger crystals are dark purplish red by transmitted light. It is almost insoluble in water; very slightly soluble in hydrochloric acid. It is best dissolved in

hot dilute hydrochloric acid, giving a reddish yellow solution, a decided yellow on dilution. The aqueous solution somewhat decomposed on boiling. The usual ruthenium reactions were given with potassium thiocyanate, and with ammonia and thiosulphate. The purple of this latter reaction comes more quickly than with the trichloride salts.

1. Filtrates from $\text{Cs}_2\text{RuO}_4\text{Cl}_4$ (formed from RuO_4 , CsCl , and HCl), boiled with hydrochloric acid, precipitated by alcohol as buff powder and recrystallized from hydrochloric acid, 0.2171 gram.

2. The alcoholic filtrate (similar to 1) evaporated somewhat giving on cooling black and red ($\text{Cs}_2\text{Ru}(\text{OH}_4)\text{Cl}_4$) crystals, extracted with warm hydrochloric acid in which red crystals are more soluble, 0.4220 gram.

3. From 2 by further evaporation. Resembles black sand, 0.6118 gram.

4. From $\text{Cs}_2\text{Ru}(\text{OH}_4)\text{Cl}_4$ (rose prisms) by boiling with concentrated hydrochloric acid. Contains small amount of trichloride, 0.2038 gram.

	1.	2.	3.	4.	Theory.
Ruthenium	17.69	17.94	17.64	17.51
Chlorine (with ruthenium) ..	23.76	22.54	24.05	22.11	24.44
Cesium	46.63	46.00	45.59	45.82
Chlorine (with cesium)	12.42	12.27	12.16	12.22

Rubidium Chlororuthenate, Rb_2RuCl_6 .—Octahedra, similar to the cesium salt.

5. Crystallized out of evaporated alcoholic filtrate from precipitation of salt formed by warming RuO_4 with RbCl and strong hydrochloric acid, 0.2914 gram.

	5.	Theory.
Ruthenium.....	21.20	20.93
Chlorine (with ruthenium).....	28.78	29.22
Rubidium	35.12	35.24
Chlorine (with rubidium).....	14.99	14.61

Cesium Oxychlororuthenate, $\text{Cs}_2\text{RuO}_4\text{Cl}_4$, or $2\text{CsCl}_2\text{RuO}_4\text{Cl}_4$.—Dark reddish purple powder; under microscope regular octahedra. Decomposed instantly by water, giving black precipitate. Soluble in cold hydrochloric acid to rose solution; evolves chlorine with hot hydrochloric acid; decomposed by sulphuric acid and nitric acid, giving odor of RuO_4 (O_2 ?); deflagrates slightly on heating. Formed by the action of cesium chloride and dilute hydrochloric acid on RuO_4 with little water.

6. First crop of crystals, 0.2955 gram.

7. Second crop, 0.3635 gram.

8. 6 and 7 mixed, 0.4538 gram.

	6.	7.	8.	Theory.
Ruthenium	20.51	21.76	18.86	18.76
Chlorine (with ruthenium) ..	12.91	13.72	13.11
Cesium	48.29	48.76	49.18	49.11
Chlorine (with cesium).....	12.25	12.45	13.12	13.11
Oxygen.....	5.91

Rubidium Oxychlororuthenate, $\text{Rb}_2\text{RuO}_2\text{Cl}_4$.—Similar to cesium salt. Formed in a similar manner, except in closed vessel. Second crop of crystals, washed with hydrochloric acid.

9. Heated in oxygen with silver coils and phosphorus pentoxide tubes, 0.2843 gram.

10. Heated in hydrogen, 0.2995 gram.

	9.	10.	Theory.
Ruthenium	22.09	22.70	22.76
Chlorine (with ruthenium) ..	15.78	16.07	15.88
Rubidium	38.80	38.43	38.31
Chlorine (with rubidium)	16.09	15.93	15.88
Oxygen	6.53	7.17

In 9 the increase in weight in the phosphorus pentoxide tube was 0.0021 gram. The formula $\text{Rb}_2\text{Ru}(\text{OH})_2\text{Cl}_4$ would have required 0.0114 gram.

In 10 the oxygen was determined by loss of weight in hydrogen less chlorine given off.

Cesium Aquochlororuthenate, $\text{Cs}_2\text{Ru}(\text{OH})_2\text{Cl}_6$ or $2\text{CsCl}\cdot\text{Ru}(\text{OH}_2)\text{Cl}_3$.—Rose prisms several millimeters long, no end faces, extinction parallel to edges of prism, when fine, as when precipitated by alcohol, a buff powder. Very slightly soluble in water, more soluble in hydrochloric acid to rose solution, pink on dilution. Crystallizes unchanged from solution in hydrochloric acid, but evaporated with hydrochloric acid on water-bath is partly converted into Cs_2RuCl_6 .

11. Precipitated by alcohol from blue filtrate from electrolytically reduced RuCl_4 and CsCl ; buff powder, 0.1493 gram.

12. From evaporated filtrate after partial precipitation of Cs_2RuCl_6 (Analysis 1) by alcohol. Rose prisms, 0.2636 gram.

	11.	12.	Theory.
Ruthenium.....	17.88	18.25	18.07
Chlorine (with ruthenium)	18.93	18.76	18.90
Cesium.....	47.48	46.93	47.23
Chlorine (with cesium)	12.67	12.52	12.60
Water (by loss).....	2.97	3.74	3.20

Cesium Ruthenium Trichloride, $\text{Cs}_2\text{RuCl}_4 \cdot \text{H}_2\text{O}$ or $2\text{CsCl} \cdot \text{RuCl}_4 \cdot \text{H}_2\text{O}$.—Dark brown powder; under the microscope, tables, probably orthorhombic; when thin, brown; when thicker, dark brownish red. Some crystals one or two millimeters long exhibit base, pinacoids and dome. The chemical properties are those of ordinary salts of ruthenium trichloride. Fairly soluble in water and hydrochloric acid.

13. Formed by action of RuO_4 on hydrochloric acid and addition of cesium chloride. Recrystallized from dilute hydrochloric acid. Analysis in oxygen with phosphorus pentoxide tubes, 0.4019 gram.

	13.	Theory.
Ruthenium	18.61	18.07
Chlorine (with ruthenium)	19.11	18.90
Cesium	47.23
Chlorine (with cesium)	12.60
Water (by phosphorus pentoxide) .	3.28	3.20

Rubidium Ruthenium Trichloride, $\text{Rb}_2\text{RuCl}_4 \cdot \text{H}_2\text{O}$, or $2\text{RbCl} \cdot \text{RuCl}_4 \cdot \text{H}_2\text{O}$.—Properties and formation similar to cesium salt.

14. RuO_4 treated with concentrated hydrochloric acid and RbCl cold; recrystallized from hydrochloric acid, 0.3235 gram.

15. Same method but warm hydrochloric acid; recrystallized, 0.2925 gram.

16. Same method, warm hydrochloric acid; minute brown transparent tables, not recrystallized, 0.2598 gram.

17. Same, recrystallized, analysis in oxygen with phosphorus pentoxide tubes, 0.2480 gram.

18. RuO_4 precipitated as hydrated oxide by alcoholic potash. Precipitate dissolved in hydrochloric acid and RbCl added to hot solution. Crystallized out on cooling. Heated to 260° two hours. A subsequent experiment showed that this salt continued to lose weight very slowly at 260° during upwards of a week and only becomes constant when one atom of chlorine has been given off, 0.2027 gram.

	14.	15.	16.	17.	18.	Theory.
Ruthenium	22.13	22.46	22.25	23.15	22.39	21.73
Chlorine (with ruthenium)	22.90	22.42	23.37	23.01	23.09	22.74
Rubidium.....	37.88	36.27	37.45	35.78	37.17	36.48
Chlorine (with rubidium) ..	15.71	15.66	14.45	14.83	15.41	15.19
Water	2.26 ¹	3.18 ¹	2.08 ¹	2.66 ²	4.58 ³	3.85

¹ By difference.

² By phosphorus pentoxide.

³ 3.11 at 260° + 1.47 by difference.

Complex Cesium Salts of Ruthenium Trichloride.—Analyses give evidence of the existence of a number of these salts, though the formulas cannot be considered as established, as there is no certainty that the substance analyzed was completely uniform. Analyses of three of these salts are appended.

19. Fine brown powder, precipitated by cesium chloride from a solution of RuO₃ in concentrated hydrochloric acid, 0.5496 gram.

20. Minute brown crystals precipitated by alcohol from the filtrate from 19, 0.0744 gram.

They both correspond most closely to the formula $3\text{CsCl}_2\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$.

	19.	20.	Theory.
Ruthenium.....	19.81	20.97	20.84
Chlorine (with ruthenium).....	22.04	20.37	21.81
Cesium.....	41.63	42.74	40.91
Chlorine (with cesium).....	11.10	11.43	10.90
Water (by loss).....	5.37	4.09	5.54

21. Black crystals, seemingly uniform octahedra, crystallized on cooling from a strongly acid solution of hydrated oxide of ruthenium and cesium chloride in hydrochloric acid, 0.1217 gram.

Corresponds best to $3\text{CsCl}_2\text{RuCl}_3 \cdot \text{H}_2\text{O}$.

	21.	Theory.
Ruthenium	20.53	21.64
Chlorine (with ruthenium).....	22.72	22.65
Cesium	42.28	42.46
Chlorine (with cesium).....	11.27	11.33
Water (by loss)	1.20	1.91

22. Brown powder, on evaporation of filtrate from 12, 0.1774 gram.

23. Dark chocolate brown powder. Buff alcoholic precipitate from warmed RuO₃, CsCl, and dilute hydrochloric acid, dissolved in dilute hydrochloric acid and evaporated nearly to dryness. Deposited from hot solution during evaporation, 0.1209 gram.

22 and 23 correspond best to the formula $5\text{CsCl}_3\text{RuCl}_3 \cdot \text{H}_2\text{O}$.

	22.	23.	Theory.
Ruthenium.....	20.41	20.02	20.54
Chlorine (with ruthenium).....	21.00	21.45	21.50
Cesium.....	45.46	45.45	44.79
Chlorine (with cesium).....	12.12	12.12	11.94
Water (by loss).....	1.01	1.38	1.21

Lower Chloride of Ruthenium, RuCl₃(?).—The following

analyses are given to indicate the composition of the blue solution formed on the electrolytic reduction of ruthenium trichloride. The concentrated solution was either added to a strong solution of cesium chloride, or vice versa, with or without the addition of alcohol. The precipitate was immediately filtered on a Hirsch funnel and washed with dilute hydrochloric acid and alcohol, and dried on a tile.

	24.	25.	26.	27.	28.
Ruthenium	24.16	22.40	17.30	18.56	18.02
Chlorine (with ruthenium).....	16.15	16.39	17.11	17.46	15.80
Cesium	43.96	43.89	50.01	49.75	50.51
Chlorine (with cesium)	11.73	11.78	13.35	13.27	13.46
Water (by loss).....	4.18	4.22	3.37	3.16	4.91
Ratio Ru : Cl (with Ru).....	I:I.9	I:2.1	I:2.84	I:2.7	I:2.5
Ratio Cl (with Cs) : Cl (with Ru)	I:I.4	I:I.4	I:I.27	I:I.3	I:I.17
Weight of analysis.....	0.1672	0.2188	0.1289	0.1794	0.2714
		29.	30.		
Ruthenium.....		23.43	22.23		
Chlorine (with ruthenium).....		21.65	21.54		
Rubidium		34.02		
Chlorine (with rubidium).....		14.13		
Water (by loss).....		2.89	2.72		
Ratio Ru : Cl (with Ru).....		I:2.64	I:2.77		
Ratio Cl (with Rb) : Cl (with Ru)		I:I.53		
Weight of analysis.....		0.1626	0.2168		

Except in the case of 24 and 25 there is evidently no approximation to a definite compound, the substances being varying mixtures of $2\text{CsCl}_2\text{RuCl}_3\cdot\text{H}_2\text{O}$ with a reduced chloride. 24 and 25 would indicate that the composition of this chloride is $3\text{CsCl}_2\text{RuCl}_3\cdot\text{H}_2\text{O}$, or if Joly's supposition is correct, $3\text{CsCl}_2\text{Ru}(\text{OH})\text{Cl}_3$. The theoretical composition of the former salt is

Ruthenium	22.93
Chlorine (with ruthenium).....	16.00
Cesium	45.00
Chlorine (with cesium).....	12.00
Water	4.06

but in spite of the tolerable agreement of Analyses 24 and 25, the formula cannot be considered as established, and it is hoped that by varying the conditions of its preparation, a salt of assured purity may be obtained.

WASHINGTON AND LEE UNIVERSITY,
LEXINGTON, VA.
August 20, 1901.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE.]

ON α -OXYBENZYLIDENE ACETOPHENONE.

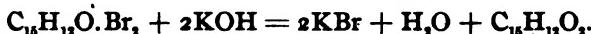
BY F. J. POND, H. J. YORK, AND R. L. MOORE.

Received August 2, 1921.

It has been shown in a previous paper¹ that when benzylidene acetophenone dibromide, $C_{15}H_{12}OBr_2$, is treated with sodium alcoholate, it is readily converted into a compound, $C_{15}H_{12}O_2$, which is identical in all respects with the substance long known as *dibenzoyl methane*. The latter compound was first prepared by Baeyer and Perkin² by boiling dibenzoyl acetic acid ester with water during several hours; it was subsequently studied by Claisen,³ who obtained it by the action of metallic sodium or sodium ethylate upon a mixture of acetophenone and benzoic acid ester. This compound was represented as a β -diketone, having the formula



Almost simultaneous with the publication of the above-mentioned paper in this Journal, J. Wislicenus⁴ published an article "On the Isomeric Forms of Dibenzoyl Methane." According to Wislicenus, two molecular proportions of potassium or sodium hydroxide dissolved in alcohol react with benzylidene acetophenone dibromide in accordance with the equation



The product, $C_{15}H_{12}O_2$, consists of a mixture of two isomeric compounds of the same melting temperature, one of which is identical with Baeyer and Perkin's, and Claisen's dibenzoyl methane; this compound is unsaturated, and Wislicenus designates it as *α -oxybenzylidene acetophenone*,



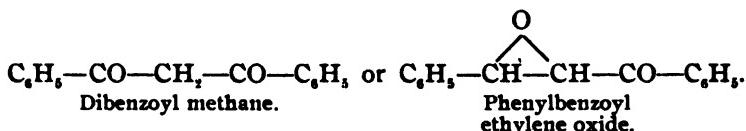
The second isomeric compound, $C_{15}H_{12}O_2$, is saturated, and may prove to be the true dibenzoyl methane or, possibly, a substance having a molecule constituted like ethylene oxide,

¹ Pond, Maxwell, and Norman: This Journal, 31, 935.

² Baeyer and Perkin: Ber. d. chem. Ges., 16, 2134; J. Chem. Soc. (London), 47, 250.

³ L. Claisen: Ber. d. chem. Ges., 30, 635; Ann. Chem. (Liebig), 291, 52.

⁴ J. Wislicenus: Ann. Chem. (Liebig), 308, 219.



Since in our previous experiments on the action of sodium methylate upon benzylidene acetophenone dibromide only one compound was obtained, it seemed desirable to continue this investigation and to compare this compound with those described by Wislicenus.

The results of this investigation indicate that sodium methylate reacts in a manner somewhat different from that of alcoholic potash ; and that the substance formed in this reaction, which was called dibenzoyl methane in the previous paper and was proved to be identical with the compound described under this name by Claisen, should be termed α -oxybenzylidene acetophenone.

EXPERIMENTAL.

Benzylidene Acetophenone, $\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{CO}-\text{C}_6\text{H}_5$.—This compound is most conveniently prepared according to the method of Claisen¹ by the action of a small quantity of a 20 per cent. solution of sodium methylate upon a mixture of the molecular proportions of acetophenone and benzaldehyde. Claisen purified this product by repeated crystallizations from petroleum ether ; this method is slow and rather unsatisfactory, since the compound is not easily soluble in this solvent, and it requires a number of recrystallizations to remove oily impurities. It was found that it could be purified readily and quickly by crystallizing from alcohol ; it separates in large crystals, melting at 57° to 58°.

α - and β -*Benzylidene Acetophenone Dibromides*, $\text{C}_{16}\text{H}_{12}\text{O.Br.}$.—By the addition of one molecular proportion of bromine to a solution of benzylidene acetophenone in chloroform, Claisen² obtained a dibromide, melting at 156° to 157°, which is difficultly soluble in cold alcohol. J. Wislicenus³ also mentions that benzylidene acetophenone is almost completely precipitated from its chloroform solution, on the addition of one molecule of bromine, as a very difficultly soluble dibromide,



¹ Claisen and Claparède : *Ber. d. chem. Ges.*, 14, 2463.

² Claisen : *Ber. d. chem. Ges.*, 14, 2463.

³ J. Wislicenus : *Ann. Chem. (Liebig)*, 308, 223.

after one crystallization from boiling alcohol, it is obtained in snow-white, pure crystals, melting at 156.5° to 157.5° . Hitherto, no mention appears to have been made of an isomeric dibromide and it is quite probable that it has been overlooked, although it is formed in small quantity whenever benzylidene acetophenone unites with bromine.

If a solution of 25 grams of benzylidene acetophenone in 125 cc. of ether be treated gradually with 20.8 grams (2 atoms) of bromine, and, after standing for a few minutes, the almost colorless solution is filtered by means of the pump from the thick, white precipitate, a considerable quantity of the new isomeric dibromide is obtained from the filtrate. The difficultly soluble compound is washed well with ether, crystallized from alcohol, and obtained as the pure white dibromide, melting at 157.5° .

The analysis gave :

- I. 0.1632 gram gave 0.1660 gram silver bromide.
- II. 0.1510 gram gave 0.1530 gram silver bromide.

	Calculated for $C_{15}H_{12}O.Br_2$	Found.	
	I.	II.	III.
Bromine.....	43.48	43.29	43.12

It is sparingly soluble in alcohol and ether, and will be termed α -benzylidene acetophenone dibromide in order to distinguish it from the lower melting, more soluble isomeric or β -dibromide.

The ethereal solution and wash-ether are treated with a small quantity of sulphurous acid in order to remove any slight excess of bromine, then washed well with water, and the ether allowed to evaporate ; the new β -dibromide is obtained from the residue. The latter is extracted with a limited quantity of boiling alcohol in order to separate a very small quantity of the comparatively insoluble α -compound, and, after evaporation of the alcohol, the β -dibromide is repeatedly crystallized from boiling alcohol. It separates in aggregates of small, fine needles, which melt at 108° to 109° . We usually obtained 3 to 4 grams of the β -dibromide by this method. It was analyzed with the following results :

- I. 0.2002 gram gave 0.3570 gram carbon dioxide and 0.0635 gram water.
- II. 0.3400 gram gave 0.3471 gram silver bromide.
- III. 0.3436 gram gave 0.3509 gram silver bromide.

	Calculated for $C_{15}H_{12}O.Br_2$	I.	Found.	
		II.	III.	
Carbon.....	48.91	48.63
Hydrogen.....	3.26	3.47
Bromine.....	43.48	43.44	43.45

It dissolves at 30° in 106 parts of ethyl alcohol, 96.7° Tr., while the α -dibromide, at the same temperature, requires 61 $\frac{1}{2}$ parts of alcohol. It is also more readily soluble in ether than the α -compound. On raising the temperature about 20° above its melting-point and then allowing to solidify, it again melts at 108.5°.

The crystalline forms of the two dibromides are quite distinct, the α - separating in short prisms, while the β -derivative crystallizes in fine needles.

It has also been observed that on brominating smaller quantities (about 5 grams) of benzylidene acetophenone at a time, and by adding the bromine rapidly, without cooling, a larger yield of the β -compound results. Although we usually employed ether as the solvent for the benzylidene acetophenone, nevertheless the formation of the isomeric bromide takes place when chloroform, carbon tetrachloride, or carbon disulphide is used. In all cases, however, the sparingly soluble α -dibromide (m. p. 157.5°) constitutes the chief product.

When the α -dibromide is heated under pressure with ethyl or methyl alcohol, hydrobromic acid is eliminated, but as yet no definite crystalline derivatives have been obtained which correspond with those so readily formed by merely boiling anisylidene acetophenone dibromide with ethyl or methyl alcohol.¹ On heating 20 grams of the α -dibromide with 100 cc. of methyl alcohol for three hours at 120°, a substance resulted which melted at 117° to 119°; this product has not, however, proved to be a definite chemical compound, and will be further studied. The change appears to take place between 110° and 125°; on heating the α -dibromide with methyl alcohol at a temperature below 110°, the unchanged compound is recovered; above 125° the substance suffers decomposition.

The Action of Two Molecules of Sodium Methylate upon the α -Dibromide.—To a solution of sodium methylate (8 grams of sodium in 200 cc. of methyl alcohol), 50 grams of α -benzylidene acetophenone dibromide were added, and boiled for thirty minutes in a reflux apparatus. Three hundred and fifty cc. of water were then introduced and the liquid rendered neutral or very slightly acid with dilute acetic acid. The oil which separated was extracted with ether, washed well with water, and dried over

¹ Pond and Shoffstall: This Journal, 22, 668 and 670.

anhydrous sodium sulphate. After evaporation of the ether, some of the oil was distilled under diminished pressure; it boiled at 206° to 210° under 12 mm. pressure, yielding a mobile, yellow oil, which had a slight odor of decomposition; it did not become solid after standing in a closed vessel for several months. Analysis of this distillate gave the following results:

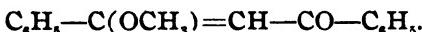
- I. 0.2243 gram gave 0.6360 gram carbon dioxide and 0.1345 gram water.
 II. 0.1978 gram gave 0.5609 gram carbon dioxide and 0.1226 gram water.

Analysis of oil prepared as above described, but which was not distilled, gave:

- III. 0.1761 gram gave 0.5059 gram carbon dioxide and 0.0975 gram water.
 IV. 0.1448 gram gave 0.4173 gram carbon dioxide and 0.0792 gram water.

	Calculated for $C_{16}H_{14}O_2$.	Found.		
		I.	II.	III.
Carbon	80.64	77.33	77.34	78.36
Hydrogen	5.88	6.66	6.93	6.15

It was thought that the action of the sodium methylate consisted in removing one molecule of hydrogen bromide from the α -dibromide and replacing the remaining bromine atom with the methoxyl group, thus giving rise to the unsaturated methyl ether of α -oxybenzylidene acetophenone,



It has been impossible, however, to obtain analyses of this oil which would agree more closely with the calculated values for the methyl ether, although many analyses have been made on various samples of the oil purified by different methods. It is clear, therefore, that the oil is not a pure ether, but in the light of subsequent experiments it seems rather probable that the oil consists of a mixture of the ether with some compound, possibly derived from it. The oil reacts as an unsaturated compound; its alcoholic solution at once decolorizes a permanganate solution; when dissolved in ether it absorbs bromine, but on evaporation of the solution hydrobromic acid is eliminated and a non-characteristic oil is obtained.

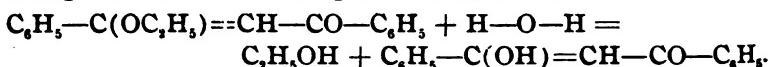
If the oil is the methyl ether suspected, or consists to some extent of this compound, it would be expected that dilute acids would convert it by hydrolysis into α -oxybenzylidene acetophenone. The following experiment indicates that this reaction actually does take place.

Some of the oil was placed into a flask and treated with fairly

concentrated hydrochloric acid ; in a very short time (one or two minutes) the entire quantity of oil was converted into the solid α -oxy-compound (m. p. 77° to 78°). This was repeated with different mineral acids of varying strength, also with acetic acid, and it was found that the oil was in each case converted into the solid compound, although with very dilute acids the action requires a longer time for its completion. On standing in an open dish in the laboratory the change is more gradual, but in a month's time the oil is almost completely converted into the solid α -oxy-compound. If this oil be placed in a closed vessel, it may be kept unchanged for a long time. We have retained a specimen in a desiccator, over fused calcium chloride, for nine months without the least trace of a solid being formed ; when, however, a drop of it was brought in contact with dilute acid, it was almost immediately changed into the solid compound.

When α -benzylidene acetophenone dibromide was treated with 2 molecules of sodium *ethylate* in the same manner as with the methylate, a reddish colored oil resulted ; this oil was analyzed with results similar to those above mentioned. It has properties similar to those of the oil resulting by the methylate treatment, decomposes on distillation at atmospheric pressure, distils with slight decomposition under reduced pressure, and is converted into α -oxybenzylidene acetophenone by contact with acids. It may contain the unsaturated ethyl ether of α -oxybenzylidene acetophenone, as indicated by the following experiment.

Eight grams of the red oil, previously well washed with water, dried over calcium chloride, and maintained for some time at 110°, were treated with 32 cc. of hydrochloric acid (1 : 1) ; in a short time the oil was converted into a solid, with a slight evolution of heat. The solid was filtered off, crystallized from alcohol and recognized as α -oxybenzylidene acetophenone, melting at 77°; the presence of ethyl alcohol in the filtrate was readily and distinctly determined by means of the iodoform reaction. This change is doubtless to be represented by the formula



That is, the oil undoubtedly contains the ethyl ether which is hydrolyzed by dilute acids, yielding ethyl alcohol and the α -oxy-compound.

α -Oxybenzylidene Acetophenone, $C_9H_8-C(OH)=CH-CO-C_6H_5$.—This compound is readily obtained in good yield by treating the oil which results from the action of 2 molecules of sodium alcoholate upon α -benzylidene acetophenone dibromide with fairly concentrated hydrochloric acid. It is also easily formed by boiling the oil with acetic acid and then precipitating with ice-water. The crude product melts at 76° to 77° , and frequently has a slight yellow to reddish tinge. It is best purified by conversion into its copper salt and decomposition of the latter by dilute hydrochloric acid. It crystallizes well from methyl or ethyl alcohol; when the alcoholic solution is fairly concentrated, the crystals are obtained in the form of long needles, but from dilute solutions it separates in large plates or tablets; the latter form of crystals are also obtained from ether. Both modifications melt sharply at 77° to 78° , thus confirming J. Wislicenus¹ observations regarding the melting-point of the so-called dibenzoyl methane. Analysis gave the results :

- I. 0.2895 gram gave 0.8530 gram carbon dioxide and 0.1380 gram water.
 II. 0.2997 gram gave 0.8880 gram carbon dioxide and 0.1500 gram water.

	Calculated for $C_{15}H_{12}O_2$.	Found.
Carbon.....	80.36	I. 80.35 II. 80.80
Hydrogen.....	5.35	5.29 5.56

It may be noted here that this compound agrees completely in properties with the substance described by J. Wislicenus as α -oxybenzylidene acetophenone (formerly called dibenzoyl methane), but in no case have we obtained a trace of the isomeric compound observed by Wislicenus. It reacts readily with an alcoholic solution of copper acetate, forming the *copper salt*,² $C_{20}H_{16}O_4Cu$; this is insoluble in alcohol and ether, and only sparingly soluble in chloroform and benzene. It melts at 294° to 301° with decomposition.

The *iron salt* is precipitated on the addition of molecular quantities of ferric chloride and sodium acetate to an alcoholic solution of the α -oxy-compound; it is obtained in the form of a brick-red powder.

When a solution of α -oxybenzylidene acetophenone is boiled with 2 molecular proportions of hydroxylamine hydrochloride,

¹ J. Wislicenus: *Ann. Chem. (Liebig)*, 308, 228.

² J. Wislicenus: *Ibid.*, 308, 231.

$\alpha\gamma$ -diphenyl isoxazole,¹ C₁₅H₁₁NO, is formed ; it separates from alcohol in brilliant, white leaflets, and melts at 141° to 142°. The same compound results on treating the alcoholic solution of α -benzylidene acetophenone dibromide with aqueous solutions of hydroxylamine hydrochloride and potassium hydroxide ; it crystallizes from alcohol and melts at 141.5°.

On the addition of one molecule of bromine to a solution of the α -oxy-compound in chloroform, hydrogen bromide is given off and *mono*-brom dibenzoyl methane,² C₁₅H₁₁BrO₂, is produced. It separates from alcohol in fine, white crystals, melting at 91.5° to 92.5°.

On boiling β -benzylidene acetophenone dibromide with sodium alcoholate it was thought that a compound isomeric with α -oxy-benzylidene acetophenone, and possibly identical with Wislicenus' second compound, might result ; this does not, however, appear to be the case. Ten grams of the β -dibromide were treated as usual with 2 molecules of sodium methylate ; after adding water and carefully neutralizing with dilute acetic acid, the resultant oil was extracted with ether, dried with anhydrous sodium sulphate, and the ether evaporated. The oil was then boiled for a short time with acetic acid and poured into ice-water ; it solidified rapidly and crystallized from alcohol in long needles, melting at 77° to 78° ; it separated from ether in plates of the same melting-point. In alcoholic solution it gave an immediate deep purple coloration with ferric chloride, and was quantitatively converted into the green copper salt by the addition of an alcoholic solution of copper acetate. It is therefore identical with the above described α -oxybenzylidene acetophenone.

In the future we propose to investigate more thoroughly the new β -dibromide, and to ascertain whether it is possible to convert this compound into an isomeric modification of benzylidene acetophenone.

¹ J. Wislicenus : *Ann. Chem. (Liebig)*, 308, 248 ; see also Goldschmidt : *Ber. d. chem. Ges.*, 28, 2540.

² Neuville and Pechmann : *Ber. d. chem. Ges.*, 23, 3377 ; J. Wislicenus : *Ann. Chem. (Liebig)*, 308, 247.

ON POSITIVE AND NEGATIVE HALOGEN IONS.

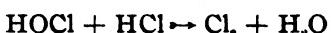
BY JULIUS STIEGLITZ.

Received August 9, 1902.

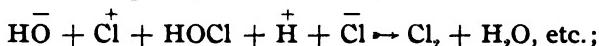
AT the end of an article on "The Reaction between Chlorine and Ammonia," published by W. A. Noyes and A. C. Lyons in a recent number of this Journal,¹ the interesting suggestion is made, that the chlorine may dissociate, before action, into positive as well as negative ions; the suggestion is accompanied by an invitation for discussion and further consideration.

The writer is induced to open the discussion because for a number of years the hypothesis of the existence of positive as well as negative ions of the three halogens, chlorine, bromine, and iodine, and notably of the formation of positive halogen ions by hypochlorous, hypobromous, and hypoiodous acids, with its consequences, has been publicly presented before the student and the professional body at the University of Chicago. The theory was supported, among other things, by the behavior of the above hypo-acids towards acids and by the strongly marked basic properties of the iodoso² and iodonium bases.³

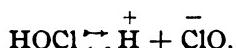
As far as the former is concerned, the reaction



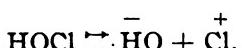
was considered as a purely ionic reaction,



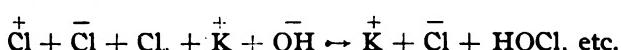
hypochlorous acid ionizes very little but, like so many nearly neutral hydroxides, it ionizes both as a weak acid,



and at the same time as a still weaker base,



much like aluminum hydroxide, the relative size of whose ionization constants is reversed. In the same way the action of chlorine on alkalies in aqueous solution was considered as a purely ionic reaction :



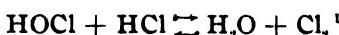
¹ This Journal, 23, 463.

² Willgerodt : *Ber. d. chem. Ges.*, 23, 3494, etc.; V. Meyer : *Ibid.*, 23, 2632, etc.

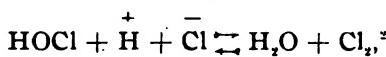
³ Hartmann and V. Meyer : *Ibid.*, 27, 426, etc.

The chief object of these lines is, however, to point out that the existence of *positive chlorine ions*, in aqueous solutions both of chlorine and of hypochlorous acid, can no longer be considered as a mere hypothesis, but must be accepted as proved experimentally by the splendid, quantitative experiments of Jakowkin¹ on the action of water on chlorine, although this consequence of his work has not heretofore been recognized.

Jakowkin's experiments prove conclusively that the reaction



is reversible; and also that it is an *ionic* reaction. A condition of equilibrium is produced according to



and is dependent consequently on the concentrations of the hydrogen and chlorine ions as well as of the hypochlorous acid and chlorine. It is obvious, however, that if the reaction as far as the hydrochloric acid is concerned is an ionic one (which is rigidly proved) and also as far as the water is concerned (which is universally recognized); it must of necessity be an ionic reaction also for the *hypochlorous acid* (which must therefore dissociate, at least to a very slight extent, into hydroxyl and *positive chlorine ions*), and also be an ionic reaction for *chlorine*, which must dissociate partially into *positive* and negative ions. The very cause of hydrolysis as in all such cases and of the reversibility lies, not more in the minimal, but actual, ionization of water, than in the formation of these ions of hypochlorous acid and of chlorine, if the theory of ionization means anything at all.

It is curious that neither Jakowkin, nor any of the chemists who have commented on his work, seem to have drawn this obvious conclusion from it,—in the author's opinion the most important truth growing out of his fine experiments. Jakowkin assumes in his calculations that the hypochlorous acid is not dissociated into ions. Its dissociation constant undoubtedly is so small that, as in the case of water, it may well be neglected in these calculations; but, as in the well established ionization of water, no matter how small the ionization constant for hypochlorous acid, it must be taken into account.

¹ *Ztschr. phys. Chem.*, 29, 613.

² Substances occurring in minimal quantities, e. g., the ions of water, chlorine and hypochlorous acid, are, for the sake of simplicity, not represented in the equation.

rous acid (for $\text{HO} + \text{Cl}$) may be, it involves the *fact* of the existence of *positive chlorine ions*.

It must be added that these views would have been published long ere this, if it had not been the hope of the author to report at the same time on other direct experimental confirmations of them. Circumstances have made it impossible to undertake before this the delicate work involved; but in the ensuing year it is intended at least to study the behavior, of solutions of chlorine, hypochlorous acid, iodine chloride, etc., towards the electric current, in the hope of proving that, under suitable conditions, the migration of positive halogen ions to the negative pole will take place. Such a migration would decide the question, it seems to me, in the most direct and unquestionable fashion. I regret that the interesting paper of Professor Noyes and Mr. Lyons has made it necessary to publish these lines rather prematurely; but their invitation for discussion encourages me to do so before the completion of my own experiments.

UNIVERSITY OF CHICAGO,
August 3, 1901.

THE PHOTOMETRIC DETERMINATION OF SULPHATES.

BY D. D. JACKSON.

Received September 3, 1901.

THE time element enters largely into most transactions in the industrial world and chemistry as a pure science is not always to be considered. Exact methods, if time-consuming, must give place, in many cases, to rapid tests that give practical knowledge in the shortest possible limit of time.

If a trainload of coal is detained for inspection it is not feasible to wait a day or two for an ultimate analysis by organic combustion. The heating power is obtained in an hour and a half by calorimetry. By this same process, using the Mahler bomb, the determination of volatile sulphur, which would take two hours by ordinary chemical methods, may be accomplished by photometry in five minutes,—not with great accuracy, but with sufficient accuracy for practical purposes.

The physician in analyzing urine does not desire to know the exact percentage of sulphates present, but merely to what extent the amount present is below or above the normal. Photometry tells him this in a few minutes.

The determination of sulphates as an adulterant in cement where large constructional works are being carried out may necessitate the analysis of some twenty-five samples of cement daily. This is impractical, if not impossible, by ordinary methods; but by photometry it may be easily accomplished. A limiting figure is placed upon the amount of sulphates present in the cement by the specifications of the contract and, unless the figure found is very close to that of the specifications, the photometric process is quite accurate enough. Nearly all of the determinations may be disposed of in this manner, while the questionable ones may be determined, if necessary, by more accurate gravimetric methods. In this way a needless expense of time and energy is avoided. Many other instances might be cited where the photometric determination of sulphates would be highly practical.

Professor Hinds¹ was the first to suggest the photometric analysis of precipitates, and a year ago² he published tables to facilitate this process. Since that time the author has had occasion to use this method quite extensively in the determination of sulphur and sulphuric acid, and has made at the same time a large number of gravimetric determinations to check the results. Experiments have also been made with known solutions of sulphates and with sulphuric acid. It has been found in this manner that certain modifications of Professor Hinds' method greatly increase the ease and accuracy with which these determinations may be made.

It was noted that differences in the brightness of the candle employed and differences in the distance of the candle from the bottom of the tube, as well as of the eye of the observer from the top of the tube, made appreciable differences in the results. Accordingly, a series of experiments was made to determine the process whereby the most accurate figures might be obtained. The readings in many cases were made by four different observers, so that the personal element would be eliminated. Experiments were also made with the diaphenometer of Hornung,³ modified by Parmelee and Ellms;⁴ but, while this works very well in the determination of the turbidity in water, it was not found to be as convenient or as accurate for the determination of sulphates as the

¹ This Journal, 18, 661.

² Ibid., 22, 269.

³ Eng. News, April 2, 1896.

⁴ Tech. Quart., 12, No. 2, June, 1899.

photometer of Hinds. The details of the method finally decided upon are as follows :

A very simple piece of apparatus is employed. It consists of a 100 cc. Nessler jar, 2.5 cm. in diameter, and 17 cm. to the 100 cc. mark. The dimensions need not be exact, but this is the size which is found to be most convenient. This jar is graduated from the bottom up in centimeters and millimeters to avoid constantly measuring the depth with a rule.

A standard candle is used, having just one candle power. Above this is suspended an iron ring with an indicator so that the top of the ring is always just three inches above the top of the candle itself. This brings the top of the flame in close proximity to the bottom of the tube, but just far away enough to prevent smoking or excessive heating.

The observations are made in a dark room and the candle is placed over a dark surface. The tube which is to contain the solution is enveloped in a brass holder which comes up almost to the 100 cc. mark and has a broad disk at the bottom which shields the eye from the strong light below. The bottom of this cylindrical shaped tube is entirely open except for a very narrow rim which serves to keep the glass tube in place. The inside of the holder is painted a dull black to prevent reflection.

The solution to be determined for sulphates is washed into the 100 cc. Nessler jar and made slightly acid with hydrochloric acid. Distilled water at room temperature is then added nearly to the 100 cc. mark. About 2 grams of pure solid barium chloride are added, and the solution made up exactly to the 100 cc. mark. A pure rubber stopper is placed in the top of the tube and the whole shaken thoroughly until the barium chloride is dissolved.

In a few minutes the solution is ready to be examined. The tube is placed in the brass holder and its contents are poured back and forth from the glass tube into a lipped beaker, keeping the precipitate constantly shaken up, so that throughout the liquid the turbidity is uniform.

When the holder containing the tube is placed on an iron ring suspended three inches above the top of the candle and the eye is held quite near the top of the glass tube, a point is finally reached where the flame of the candle just disappears. The height to which the solution stands in the tube (reading the bottom of the

meniscus) is then taken and from this reading the per cent. of sulphates may be calculated from the formula

$$x = \frac{0.0574}{y + 0.1},$$

where x equals grams of sulphur trioxide required, and y equals the depth in centimeters of the liquid in the cylinder.

This calculation is avoided and thereby considerable time saved by the use of the following table :

TABLE FOR THE PHOTOMETRIC DETERMINATION OF SULPHURIC ACID.

cm.	SO ₃ . Gram.	cm.	SO ₃ . Gram.	cm.	SO ₃ . Gram.	cm.	SO ₃ . Gram.
1.0	0.0522	4.0	0.0140	7.0	0.0081	10.0	0.0057
1.1	0.0478	4.1	0.0137	7.1	0.0080	10.2	0.0056
1.2	0.0442	4.2	0.0133	7.2	0.0079	10.4	0.0055
1.3	0.0410	4.3	0.0131	7.3	0.0078	10.6	0.0054
1.4	0.0383	4.4	0.0128	7.4	0.0077	10.8	0.0053
1.5	0.0359	4.5	0.0125	7.5	0.0076	11.0	0.0052
1.6	0.0338	4.6	0.0122	7.6	0.0075	11.2	0.0051
1.7	0.0319	4.7	0.0119	7.7	0.0074	11.4	0.0050
1.8	0.0302	4.8	0.0117	7.8	0.0073	11.6	0.0049
1.9	0.0287	4.9	0.0115	7.9	0.0072	11.8	0.0048
2.0	0.0273	5.0	0.0113	8.0	0.0071	12.0	0.0047
2.1	0.0261	5.1	0.0110	8.1	0.0070	12.2	0.0047
2.2	0.0250	5.2	0.0108	8.2	0.0069	12.4	0.0046
2.3	0.0239	5.3	0.0106	8.3	0.0068	12.6	0.0045
2.4	0.0230	5.4	0.0104	8.4	0.0068	12.8	0.0044
2.5	0.0221	5.5	0.0103	8.5	0.0067	13.0	0.0044
2.6	0.0213	5.6	0.0101	8.6	0.0066	13.5	0.0042
2.7	0.0205	5.7	0.0099	8.7	0.0065	14.0	0.0041
2.8	0.0198	5.8	0.0097	8.8	0.0064	14.5	0.0039
2.9	0.0191	5.9	0.0096	8.9	0.0064	15.0	0.0038
3.0	0.0185	6.0	0.0094	9.0	0.0063	15.5	0.0037
3.1	0.0179	6.1	0.0093	9.1	0.0062	16.0	0.0036
3.2	0.0173	6.2	0.0091	9.2	0.0062	16.5	0.0035
3.3	0.0168	6.3	0.0090	9.3	0.0061	17.0	0.0034
3.4	0.0164	6.4	0.0088	9.4	0.0060	17.5	0.0033
3.5	0.0159	6.5	0.0087	9.5	0.0060	18.0	0.0032
3.6	0.0155	6.6	0.0086	9.6	0.0059	18.5	0.0031
3.7	0.0151	6.7	0.0084	9.7	0.0059	19.0	0.0030
3.8	0.0147	6.8	0.0083	9.8	0.0058	19.5	0.0029
3.9	0.0144	6.9	0.0082	9.9	0.0057	20.0	0.0029

SULPHATE IN CEMENT.

Treat 1 gram of cement with strong hydrochloric acid, add water and evaporate to dryness. Add a small amount of concen-

trated hydrochloric acid, then add an equal amount of boiling water and filter into a 100 cc. graduated tube, make up to the mark with cold water, and proceed with the photometric method as directed.

If exactly 1 gram is taken, and the reading on the tube is 4.3 cm., then from the table, 1 gram contains 0.0131 gram of sulphur trioxide, or 1.3 per cent. sulphur trioxide.

Specifications usually state that not over 1.5 per cent. sulphur trioxide can be accepted. 2 per cent. is sometimes used as a limiting figure.

SULPHATE IN URINE.

Filter the urine, if turbid, and take 10 cc., make it slightly acid with hydrochloric acid and add water nearly to the 100 cc. mark. Add about 2 grams of solid barium chloride, make up to the 100 cc. mark, and proceed as directed in the method.

If 10 cc. are taken and the reading on the tube is 4.6, then from the table, 10 cc. equals 0.0122 gram sulphur trioxide, or 0.12 per cent.

Normal urine varies from 0.10 to 0.15 per cent. sulphur trioxide.

SULPHATE IN WATER.

100 cc. may be taken for well waters, but some well waters and many surface waters will need to be concentrated in order to get accurate results.

A quick determination in waters low in sulphates may be roughly made by taking 100 cc. of water, acidifying slightly with hydrochloric acid and adding solid barium chloride. After shaking well, the turbidity is compared with silica standards sidewise toward the light. These silica standards have been used in the determination of the turbidity of drinking water.¹

A standard of ten in silica is equivalent to a turbidity produced by 1.45 parts per million of sulphur trioxide. The photometric method, while not as rapid as this for solutions requiring concentration, is, however, much more accurate. The reason for this will be shown by a study of the diagram given later, in which it is seen that the results do not follow the reciprocal curve.

SULPHATE IN COAL.

After fusion by the ordinary method, the sulphate in coal may

¹ Whipple, G. C., and Jackson, D.D.: *Tech. Quart.*, 12, No. 4, Dec. 1899; 13, No. 3, Sept., 1900.

be determined photometrically ; but when the Mahler bomb is used, the volatile sulphur is all in solution in the water at the bottom of the bomb. This water is filtered and titrated with 0.1 normal sodium carbonate, using methyl orange as an indicator to get the nitric acid present. It is then ready for the determination of sulphur by photometry. The pink color of the solution does not interfere with the results.

The following is a special table calculated for the determination of sulphur :

TABLE FOR THE PHOTOMETRIC DETERMINATION OF SULPHUR.

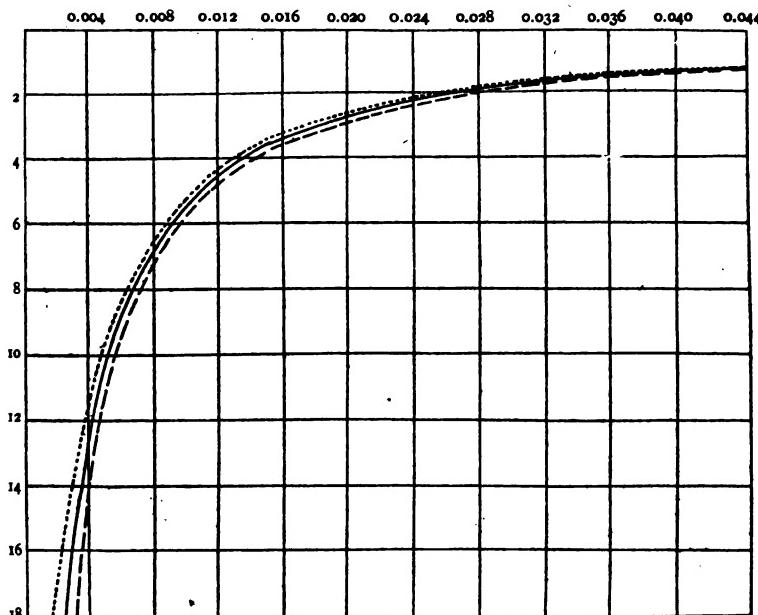
Sulphur. cm. Gram.	Sulphur. cm. Gram.	Sulphur. cm. Gram.	Sulphur. cm. Gram.	Sulphur. cm. Gram.
1.0 0.0209	4.0 0.0056	7.0 0.0032	10.0 0.0023	
1.1 0.0191	4.1 0.0055	7.1 0.0032	10.2 0.0022	
1.2 0.0177	4.2 0.0053	7.2 0.0032	10.4 0.0022	
1.3 0.0164	4.3 0.0052	7.3 0.0031	10.6 0.0022	
1.4 0.0153	4.4 0.0051	7.4 0.0031	10.8 0.0021	
1.5 0.0144	4.5 0.0050	7.5 0.0030	11.0 0.0021	
1.6 0.0135	4.6 0.0049	7.6 0.0030	11.2 0.0020	
1.7 0.0128	4.7 0.0048	7.7 0.0030	11.4 0.0020	
1.8 0.0121	4.8 0.0047	7.8 0.0029	11.6 0.0020	
1.9 0.0115	4.9 0.0046	7.9 0.0029	11.8 0.0019	
2.0 0.0109	5.0 0.0045	8.0 0.0028	12.0 0.0019	
2.1 0.0104	5.1 0.0044	8.1 0.0028	12.2 0.0019	
2.2 0.0100	5.2 0.0043	8.2 0.0028	12.4 0.0018	
2.3 0.0096	5.3 0.0042	8.3 0.0027	12.6 0.0018	
2.4 0.0092	5.4 0.0042	8.4 0.0027	12.8 0.0018	
2.5 0.0088	5.5 0.0041	8.5 0.0027	13.0 0.0018	
2.6 0.0085	5.6 0.0040	8.6 0.0026	13.5 0.0017	
2.7 0.0082	5.7 0.0040	8.7 0.0026	14.0 0.0016	
2.8 0.0079	5.8 0.0039	8.8 0.0026	14.5 0.0016	
2.9 0.0076	5.9 0.0038	8.9 0.0026	15.0 0.0015	
3.0 0.0074	6.0 0.0038	9.0 0.0025	15.5 0.0015	
3.1 0.0072	6.1 0.0037	9.1 0.0025	16.0 0.0014	
3.2 0.0069	6.2 0.0036	9.2 0.0025	16.5 0.0014	
3.3 0.0067	6.3 0.0036	9.3 0.0024	17.0 0.0014	
3.4 0.0066	6.4 0.0035	9.4 0.0024	17.5 0.0013	
3.5 0.0064	6.5 0.0035	9.5 0.0024	18.0 0.0013	
3.6 0.0062	6.6 0.0034	9.6 0.0024	18.5 0.0012	
3.7 0.0060	6.7 0.0034	9.7 0.0024	19.0 0.0012	
3.8 0.0059	6.8 0.0033	9.8 0.0023	19.5 0.0012	
3.9 0.0058	6.9 0.0033	9.9 0.0023	20.0 0.0012	

If 1 gram of coal is taken and the reading on the photometer is 3.1 cm., then from the table the amount present is 0.0072 gram, and the coal contains 0.7 per cent. of sulphur. A coal should

not contain over 1 per cent. of volatile sulphur; 1.5 per cent. may sometimes be taken as a limit.

In the accompanying diagram the long dash line is the curve produced by the precipitation of barium sulphate where the ordinates are centimeters in depth, and the abscissas are grams of sulphur tri-oxide when reading with the photometer. The unbroken line is the reciprocal curve and the dotted line is the curve produced by standard silica made from diatomaceous earth.

The silica curve shows the form of curve produced by an absolutely insoluble substance and its variation from the reciprocal curve shows the effect of the cutting out of light by the water itself.



The difference between the silica curve and the sulphate curve represents the solubility of the barium sulphate. This explains why the formula takes the form

$$x = \frac{0.0574}{y + 0.1},$$

when according to optics the denominator should be $(y - a)$ instead of $(y + a)$.

A wide field is open for experiments upon the photometric

determination of other precipitates and, in the future, there is no reason why photometry should not take as important a place in chemical analysis as that now occupied by colorimetry.

MT. PROSPECT LABORATORY,
BROOKLYN, N. Y.

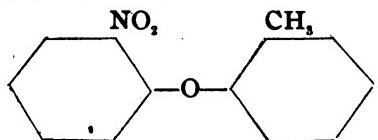
DERIVATIVES OF PHENYLETHER, II.

BY ALFRED N. COOK.

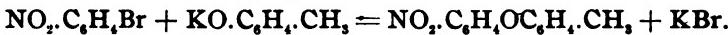
Received August 27, 1901.

In a paper¹ published a few months since by A. N. Cook and H. W. Hillyer a number of derivatives of phenylether were described which had been prepared by acting on potassium paracresolate with orthobromnitrobenzene, and reducing and oxidizing the resulting compound. During the past six months the work has been extended to orthocresol and metacresol with results as described in the following pages :

2-Nitro-2'-Methylphenylether,



This compound was prepared by the action of orthobromnitrobenzene upon potassium orthocresolate. The reaction is represented by the following equation :



The potassium orthocresolate was prepared by heating on the water-bath, for several hours, molecular equivalents of orthocresol and potassium hydroxide dissolved in a little water, and then drying in the air-bath until thoroughly desiccated. On cooling, it solidified to a crystalline mass of a light brownish color. It is very hygroscopic.

In the preparation of the ether, molecular equivalents of potassium orthocresolate and orthobromnitrobenzene were heated in an oil-bath. At 137° C., a gentle ebullition began which increased for a few minutes, although the containing flask was removed from the bath, and then gradually subsided. The temperature also rose several degrees during the action. When the action had ceased there remained a copious precipitate of potassium bromide and a supernatant brownish-black liquid. When cool the liquid was

¹ *Am. Chem. J.*, 24, 525-529.

extracted with ether. The ether extract was washed with a weak water solution of potassium hydroxide to remove any free cresol which might be present. The orthobromnitrobenzene which remained unacted upon was distilled off with steam and the phenylether was distilled under diminished pressure.¹ Fourteen grams of the crude ether were obtained from 26 grams of orthobromnitrobenzene, or 40 per cent. of theory. Twenty-six per cent. of the orthobromnitrobenzene remained unacted upon.

When two molecular equivalents of the orthobromnitrobenzene were employed to one of potassium orthocresolate, a temperature of 170° C. was required to induce reaction and the yield was much less than with equimolecular quantities. When molecular equivalents of the two reacting compounds were heated with orthocresol as a menstruum, action began at 165° C. The temperature rose to 200° C. although the containing flask was removed from the bath. On cooling, a tarry mass resulted which could not be extracted with ether and no phenylether was obtained from it. Other solvents, such as nitrobenzene, that possess a high boiling-point were used, but no reaction took place, although the temperature was raised 65° C. above the point where they react, when heated together in equimolecular quantities. The first instance would be explained by the free cresol acting on the orthobromnitrobenzene or the resulting compound. The second would be explained on the ground that no ionization of the two reacting substances takes place in the solvents used. An endeavor to prepare the substance by substituting sodium orthocresolate for the potassium compound was also unsuccessful. A tar resulted from which nothing could be extracted with ether.

2-Nitro-2'-methylphenylether is a dark red liquid of 1.195 specific gravity at 20° C. It has an oily taste, and a fruity odor which is probably due to small traces of impurities. It is soluble in organic solvents in general, but is insoluble in water; is not volatile with steam; and when subjected to a temperature of 18° C. for several hours it did not solidify. It decomposes when boiled under ordinary atmospheric pressure, but distils unchanged at 194°-196° C. under a pressure of 14 mm. 0.6925 gram of the liquid, dissolved in 41.8 grams of absolute alcohol, gave a rise of the boiling-point of 0.095°. This gives 200.6 as the molecular

¹ I am indebted to the kindness of Dr. H. W. Hillyer, of the University of Wisconsin, for distilling this compound for me under diminished pressure, as well as the 2-nitro-3'-methylphenylether mentioned farther on.

weight. Theory requires 229. Potassium dichromate in acetic acid solution does not oxidize the side-chain to carboxyl as in case of 2-nitro-4'-methylphenylether. The compound is burned completely when the temperature is but slightly raised. Analyses resulted as follows :

	Calculated for $C_{13}H_{11}NO_3$	Found.	
		I.	II.
Carbon	68.12	67.97	68.22
Hydrogen	4.83	4.50

2-Amino-2'-Methylphenylether Hydrochloride, $CH_3.C_6H_4OC_6H_4NH_2.HCl$.—The amido compound was prepared by dissolving the previously described phenylether in alcohol and reducing with tin and hydrochloric acid while warming on the water-bath. The action was allowed to continue until a test portion yielded no precipitate when diluted with a large amount of water. The tin was precipitated with hydrogen sulphide and the solution concentrated on the water-bath, when it assumed a slightly pink tint. The hydrochloride does not crystallize but simply separates out in the form of a snow-white wax which coheres readily when pressed together with the fingers. It is readily soluble in ether and alcohol, and moderately soluble in water. A water solution does not yield a chlorplatinate with hydrochloroplatinic acid. Of several attempts to prepare the amido derivative only one was successful. It would invariably decompose while concentrating on the water-bath. The specimen obtained, however, was perfectly stable. It was kept for several days, a part of the time in contact with water. In attempting to prepare the free base by precipitating with ammonia, it decomposed before it could be filtered.

2-Nitro-2'-Methylphenylether Sulphonic Acid, $NO_2C_{11}H_9O_2CH_3SO_3H$.—The free acid was prepared by dissolving 2-nitro-2'-methylphenylether in concentrated sulphuric acid, diluting with a large amount of water, precipitating the excess of sulphuric acid with lead nitrate, and removing the excess of lead with hydrogen sulphide. The solution was then evaporated on the water-bath and the acid desiccated over sulphuric acid.

It is a reddish-yellow, sirupy liquid which becomes somewhat viscous on cooling, and has an intensely bitter taste. It is readily soluble in petroleum ether, glacial acetic acid, wood alcohol, ethyl alcohol, benzene, nitrobenzene, dimethyl aniline, glycerine, aldehyde, and benzaldehyde. One part of the acid is soluble in

about 2.5 parts of water at 80° C. and considerably less soluble in cold water. A weak solution of the acid does not yield a precipitate with any of the metals. Its composition was determined by the analyses of some of its salts which are given below.

Barium Salt, ($\text{NO}_2\text{C}_{11}\text{H}_9\text{O.CH}_3\text{SO}_3$)₂Ba.—This salt was prepared by adding sufficient barium chloride to the diluted sulphuric acid solution of the ether to remove the excess of sulphuric acid and change all of the free sulphonic acid to the barium salt. Owing to the fact that the salt is only sparingly soluble in cold water, most of it was precipitated along with the barium sulphate and had to be extracted from it with boiling hot water, from which it crystallized on cooling in light, fluffy, radial aggregations of fine, cream-white needles. It is almost without taste. 7.45 parts of the salt are soluble in 1000 parts of boiling hot water and 1.2 parts are soluble in 1000 parts of water at 31° C. The water solution is almost colorless. This salt is the least soluble of any here described, and as a consequence the most easily purified. Two determinations of the barium after crystallizing the compound four times from hot water and drying at 150° C. resulted as follows:

- I. 0.2394 gram of the substance yielded 0.0731 gram of barium sulphate.
- II. 0.5112 gram of the substance yielded 0.1567 gram of barium sulphate.

	Calculated for ($\text{C}_{13}\text{H}_{10}\text{O}_6\text{SN}_2$) ₂ Ba.	Found.
	I.	II.
Barium.....	18.18	17.96 18.04

Strontium Salt, ($\text{CH}_3\text{C}_{12}\text{H}_7\text{O.NO}_2\text{SO}_3$)₂Sr + 2H₂O.—The strontium salt was prepared by the same general method as the barium salt. Strontium nitrate was used to precipitate the excess of sulphuric acid. Some of the salt was thrown down with the strontium sulphate and was extracted with hot water. It crystallizes from a hot water solution in crystalline grains except when allowed to crystallize very slowly, when the crystals resemble snowflakes in form. They are brownish yellow in color and about 2 mm. in diameter. The water solution of the salt is yellow. Twenty parts of the compound are soluble in 1000 parts of boiling hot water, and 6.8 parts are soluble in 1000 parts of water at 31° C. On being dried in the air-bath at 110° C. it lost in weight corresponding to two molecules of water.

- I. 0.2326 gram of the substance yielded 0.0104 gram of water and 0.0576 gram of strontium sulphate.

II. 0.2385 gram of the substance yielded 0.0108 gram of water and 0.0595 gram of strontium sulphate.

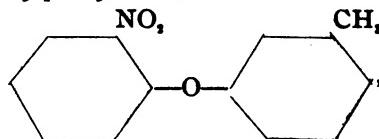
	Calculated for (CH ₃ C ₁₂ H ₇ O ₄ NO ₃ SO ₄) ₂ Sr + 2H ₂ O.	Found.
Strontium	II. 84	I. 11.82 II. 11.91
Water.....	4.87	4.47 4.53

Lead Salt, (CH₃C₁₂H₇O₄NO₃SO₄)₂Pb.—The same general method was used in the preparation of the lead salt as with the two preceding. Owing to the greater solubility, however, it was not necessary to digest the lead sulphate precipitate with hot water, but it was necessary to concentrate the solution in order to induce crystallization. Its water solution is a deep yellow. It crystallizes in well defined, yellow, crystalline grains. 81.7 parts of the salt are soluble in 1000 parts of boiling water, and 35 parts are soluble in 1000 parts of water at 31° C.

- I. 0.3600 gram of the substance yielded 0.1001 gram of lead oxide.
II. 0.2816 gram of the substance yielded 0.0766 gram of lead oxide.

	Calculated for (CH ₃ C ₁₂ H ₇ O ₄ NO ₃ SO ₄) ₂ Pb.	Found.
Lead	II. 15	I. 25.55 II. 25.24

2-Nitro-3'-Methylphenylether,



was prepared by the same general method as the 2-nitro-2'-methylphenylether described in the preceding pages, from potassium metacresolate and orthobromnitrobenzene. The potassium orthocresolate was prepared in the same manner as the potassium orthocresolate. It is a light brown crystalline solid, when prepared by this method. It melts at about 55° C., and liquefies by absorption of water when allowed to remain in contact with the air.

When the temperature of the two reacting substances was raised to 100° C. a gentle ebullition began which increased and the temperature rose to 145° C., although the containing flask was removed from the oil-bath. The action continued for about five minutes and then subsided. There remained a copious precipitate of potassium bromide and a supernatant brown liquid. The yield was almost quantitative in the first experiment but not so good in the second.

This compound is a red, oily liquid. From its appearance it could not be distinguished from 2-nitro-2'-methylphenylether. Its specific gravity is 1.208 at 27° C. It is not volatile with steam; it has an oily taste and a slight, fruity odor, probably due to small quantities of impurities; decomposes when boiled under ordinary atmospheric pressure, but under 30 mm. pressure it distils without decomposition at 223° C. It is very soluble in alcohol, ether, benzene, chloroform, acetic acid, and other organic solvents. It is insoluble in water. An attempt to oxidize the side-chain to carboxyl was unsuccessful. It seemed to burn completely. Owing to the small amount of the substance at hand I was unable to make an analysis, but its composition is sufficiently shown by the analysis of the barium salt of the sulphonic acid derivative.

2-Amino-3'-Methylphenylether Hydrochloride, $\text{CH}_3\text{C}_6\text{H}_4\text{OC}_6\text{H}_4\text{NH}_2\text{HCl}$, was prepared in the same manner as the corresponding hydrochloride of 2-amino-2'-methylphenylether. It was more stable, however, during the process of preparation, only decomposing slightly when evaporating the water solution on the water-bath. It is a clear, viscous substance, very soluble in alcohol and ether, but quite sparingly soluble in water. A water solution does not yield a precipitate with hydrochlorplatinic acid. An attempt to prepare the free base was unsuccessful. It was precipitated from its water solution with ammonia, but it decomposed under the bell-jar over sulphuric acid before it could be thoroughly dried.

2-Nitro-3'-Methylphenylether Sulphonic Acid, $\text{NO}_2\text{C}_6\text{H}_4\text{CH}_3\text{SO}_3\text{H}$, was prepared by the same method as the corresponding derivative of 2-nitro-2'-methylphenylether. On concentrating the water solution it crystallizes in short, well defined, yellowish brown needles. It possesses a slightly bitter taste, and is soluble in alcohol, ether, and other organic solvents. Its water solution is yellow and dyes the hands yellow.

The Barium Salt, $(\text{NO}_2\text{C}_6\text{H}_4\text{CH}_3\text{SO}_3)_2\text{Ba} + 2\text{H}_2\text{O}$, was prepared in the same manner as the barium salt of 2-nitro-3'-methylphenylether sulphonic acid. It separates from a weak water solution in crystals about 2 mm. in diameter which resemble snowflakes in appearance, but with a heavier structure. They are light brown in color and are composed of little balls connected to



the central portion by ligaments as shown in the accompanying drawing. Eleven parts of the salt are soluble in 1000 parts of water at 82° C. and 6.1 parts are soluble in 1000 parts of water at 35° C.

When dried in the air-bath at 100° C. for an hour it lost in weight corresponding to two molecules of water.

I. 0.2583 gram of the substance yielded 0.0110 gram of water.

II. 0.2363 gram of the substance yielded 0.0098 gram of water and 0.0683 gram of barium sulphate.

	Calculated for $(CH_3C_{12}H_7NO_2SO_4)_2Ba + 2H_2O$.	Found.
	I.	II.
Barium.....	17.36
Water	4.05	4.26 4.15

2-Nitro-4'-methylphenylether Sulphonic Acid, $NO_2C_{11}H_9O.CH_3SO_3H$, was made from the corresponding ether previously described¹ by the same method as the analogous compounds already described in this paper. The heat of the boiling water-bath was necessary to induce solution of the ether in the concentrated sulphuric acid. No charring was produced as stated in a previous article.² The substance then used, as was afterwards known, was not quite pure. On decomposing the lead salt with hydrogen sulphide and concentrating the water solution, the acid crystallizes out in well-defined crystals of a reddish brown color and a slightly bitter taste. After being desiccated over sulphuric acid it increases in weight rapidly on coming in contact with the air. Its water solution is very yellow. It is readily soluble in alcohol, ether, benzene, glacial acetic acid, and other organic solvents. Ninety-eight parts of the acid are soluble in 1000 parts of water at 31° C. Its water solution does not give a precipitate with any of the metals. Its composition was determined by analyzing the barium salt.

Barium Salt, $(NO_2C_{11}H_9O.CH_3SO_4)_2Ba + 5H_2O$.—The barium salt was prepared in the same manner as its analogues. Its solubility in water is the highest and the number of molecules of water of crystallization the greatest of any of the salts described. On account of its greater solubility it was the most difficult to purify by recrystallization. It crystallizes out in yellowish brown warts about $\frac{1}{4}$ inch in diameter on the average. It is insoluble in organic solvents in general, but is soluble in both methyl and

¹ Am. Chem. J., 24, 526.

² Loc. cit., p. 527.

ethyl alcohol containing a very little water. 691 parts of the salt are soluble in 1000 parts of water at 80° C. and 147 parts are soluble in 1000 parts of water at 27° C. On being heated in the air-bath at 100°-110° C. it becomes somewhat lighter in color and loses in weight corresponding to five molecules of water of crystallization.

0.1792 gram of the substance yielded 0.0167 gram of water and 0.0499 gram of barium sulphate.

	Calculated for $(NO_2C_{12}H_7OCH_3)_2Ba + 5H_2O$.	Found.
Barium	16.25	16.35
Water	9.54	9.33

This study is being continued and extended to the reaction between parabromnitrobenzene and the cresols.

MORNINGSIDE COLLEGE,
SIOUX CITY, IOWA,
August 10, 1901.

OPTICAL ROTATIONS OF CERTAIN TARTRATES IN GLYCEROL.

By J. H. LONG.

Received August 17, 1901.

N EARLY all active substances exhibit different rotations in different solvents. In some cases the causes of these variations, are known while in other and numerous instances no satisfactory explanation of the variable activity has yet been given. The several important factors in this variation in specific rotation have been grouped by Landolt as follows:

- a. Electrolytic dissociation in aqueous solution.
- b. Formation or breaking down of molecular aggregations.
- c. Presence of complex so-called crystal molecules in solution.
- d. Formation of hydrates or corresponding bodies with solvent.
- e. Hydrolysis.

It was pointed out by Landolt, and confirmed by Oudemans, that in dilute solutions the molecular rotations of salts of active acids are independent of the base combined with the acid, and that in salts of active bases the molecular rotations are independent of the inactive acid. This is well illustrated by the following table in which $[M]_D$ refers to the molecular rotation.

	[M] _D
(NH ₄) ₂ C ₄ H ₄ O ₆	63.0
Na ₂ C ₄ H ₄ O ₆	59.9
K ₂ C ₄ H ₄ O ₆	64.4
NaNH ₄ C ₄ H ₄ O ₆	61.7
KNH ₄ C ₄ H ₄ O ₆	63.8
KNaC ₄ H ₄ O ₆	62.4
MgC ₄ H ₄ O ₆	61.7

For a number of solutions containing thallium tartrate and thallium double tartrates, I found molecular rotations much smaller than these for the higher concentrations but approaching them on increasing dilution.¹

Hädrich, in 1893,² gave the most plausible explanation of this behavior when he showed by conductivity experiments that the variations in molecular rotation keep pace with variations in the degree of ionization. He pointed out that for many cases of dissolved active salts the molecular rotation in dilute solution is independent of the inactive ion.

From this standpoint it is of interest to note the behavior of bodies in glycerol in which solvent the degree of ionization must be relatively small. The compounds which I have examined to test this were the following : potassium sodium tartrate, potassium antimonyl tartrate, potassium boryltartrate, ammonium tartrate, ammonium hydrogen tartrate, and ammonium antimonyl tartrate. These salts were all prepared in condition of high purity and were dissolved in a special glycerol kindly prepared for me by Dr. A. G. Manns, chief chemist of Armour & Co., to whom my thanks are due. This glycerol was not only practically anhydrous but was remarkably free from traces of other bodies.

It is difficult to secure clear crystals of the ammonium antimonyl tartrate, as on concentration of the solution a gummy mass is usually obtained. But after many trials one solution deposited an abundant crop of crystals, which by determination of the antimony and the water were found to have the composition (NH₄)(SbO)C₄H₄O₆ + $\frac{1}{2}$ H₂O. Another product secured had approximately the composition (NH₄)(SbO)C₄H₄O₆ + 2 $\frac{1}{2}$ H₂O.

The tartrates of ammonium and the potassium boryltartrate were made in the laboratory by well-known methods. The following table contains the results of polarizations made partly with

¹ Am. J. Sci. and Arts, 38, 264.

² Ztschr. phys. Chem., 12, 476.

the large Landolt-Lippich instrument in a 400 mm. tube, and partly in a Laurent instrument from Schmidt and Haensch with a 200 mm. tube.

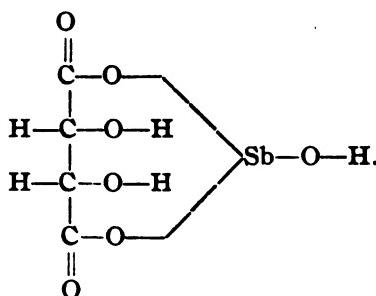
Salt.	$[\alpha]_D^{\infty}$ for water.	$[\alpha]_D^{\infty}$ for glycerol.
KNaC ₄ H ₄ O ₆ .4H ₂ O.....	22.1° c = 5 to 30	28.85° c = 5 28.35° c = 10 27.87° c = 15 27.40° c = 20 26.96° c = 25
•		
KSbOC ₄ H ₄ O ₆ . $\frac{1}{2}$ H ₂ O	140.69° c = 2	139.25° c = 2
	141.27° c = 5	141.17° c = 3
	141.40° c = 6	143.75° c = 4
KBOC ₄ H ₄ O ₆	58.10° c = 5	30.9° c = 5
(NH ₄) ₂ C ₄ H ₄ O ₆	34.50° c = 5	43.50° c = 4
(NH ₄)HC ₄ H ₄ O ₆	26.0° c = 1.5	27.7° c = 0.75
(NH ₄)SbOC ₄ H ₄ O ₆ . $\frac{1}{2}$ H ₂ O....	150.0° c = 5	146.10° c = 3 146.25° c = 4
NH ₄ SbOC ₄ H ₄ O ₆ . $\frac{1}{2}$ H ₂ O	115.7° c = 5	109.37° c = 4

It will be observed in this table that the values of the specific rotations obtained in glycerol solution for potassium sodium tartrate, ammonium tartrate and ammonium hydrogen tartrate are greater than the rotations found in aqueous solution. In the first two cases the differences are extremely marked and the active ion is probably no longer the simple group, C₄H₄O₆. It is interesting to note in the case of Rochelle salt that the specific rotation is greatest in the glycerol solution of lowest concentration, or greatest degree of separation into single molecules.

The behavior of the two antimony tartrates is the most characteristic and important. We have here very high specific rotations in water, and but slightly different in glycerol. For the first of these substances Hädrich¹ has shown that there is almost no dissociation, and it is evident that the same ion is active in both aqueous and glycerol solutions. The molecular rotations of the two bodies in water are almost identical, but for the ammonium salt the molecular rotation in glycerol is a little lower. This concordant behavior naturally suggests the existence of a peculiar acid as active in these salts, and this may be, as Clarke's investigations² of some years ago seemed to prove, a body of the formula

¹ Loc. cit.

² Am. Chem. J., 2, 319.



The heavy ion of this acid has about seven times the effect on the polarized ray that is exerted by the lighter ion of the ordinary tartaric acid in both media.

But the case is different with the potassium boryltartrate, the composition of which has usually been assumed as similar to that of the antimony compound. We have here a much lower rotation in glycerol than in water, indicating the presence of different active ions in the two media. By hydrolysis in aqueous solution, as found by Hädrich,¹ the rotation decreases very rapidly and finally approaches that of the simpler ion, $C_4H_4O_6$. It is likely therefore that this body is not perfectly analogous to tartar emetic, as in their electrical and optical behavior the arsenyl tartrates are likewise not.

It is well-known that glycerol is a remarkably good solvent for boric acid, and the low rotation of the borotartrate in that medium may possibly be accounted for by assuming that in the solution the whole or a part of the boric acid radical is withdrawn to form a glycerol compound. This kind of hydrolysis would leave then a simple tartrate. The molecular rotation calculated from the glycerol solution is almost normal which lends color to the assumption, while that from the water solution is nearly twice as great.

The main points shown then with reference to the glycerol solutions are these: The simple metallic tartrates examined dissolve in glycerol and show a larger specific rotation than in water. The antimony tartrates, which are but slightly dissociated, show nearly the same rotation in water and glycerol, and their behavior in general suggests a composition different from that usually assumed. Potassium boryltartrate shows in glycerol a much lower

¹ Loc. cit.

rotation than in water, the calculated specific rotation suggesting the presence of the simple tartrate in the glycerol solution.

NORTHWESTERN UNIVERSITY, CHICAGO
August 15, 1901.

NOTE ON THE DETERMINATION OF SILICON IN STEEL.

BY GEORGE AUCHY.

Received August 16, 1901.

ALTHOUGH it has been mentioned by Dudley that silicon results in steel by Drown's method are apt to be low, on account of the iron sulphate enclosing and protecting the silicic acid from the dehydrating action of the sulphuric acid, it is probable that this fact is one not generally appreciated by chemists.

When the method is used for pig iron, as was originally intended by its author, there is no error from this cause less,¹ but in steel the loss amounts to from 0.01 per cent. to 0.035 per cent. silicon in medium silicon (0.15 to 0.20 per cent. steels, which is too much to be ignored. Dr. Dudley thinks that it may be prevented by taking great pains to insure sufficient contact by stirring. Four experiments made by the writer, in which five minutes' stirring in each case was done after the appearance of sulphuric fumes, showed this to be true, only 0.006 per cent. silicon in each case being lost. But in a busy laboratory with many silicon determinations being made, or with much other work demanding the attention of the operator, this stirring adds considerably to the labor of the method, and the time it requires can hardly be allowed. Says Dr. Dudley: "If by some modification the iron salts could be kept in solution until the silica is rendered quite insoluble, it would apparently be a decided step forward with this method."

Several years ago the writer found that if aqua regia be used in the method instead of nitric acid alone, and the proportion of strong sulphuric acid be about 3.2 cc. per gram of drillings,² the iron salt in that case did not separate out until just a little before

¹ There is loss, it is true, of about 0.10 to 0.15 per cent. silicon in high silicon pig, but it is due to the same cause (whatever this cause may be) that in silicate analysis brings the result too low. It is a well-known fact that from 1.5 to 3 per cent. of the total silica of silicates remains in the filtrate from the first silica separation, no matter what method of dehydration be employed, or how many evaporation be made before filtration (Cameron: *Chem. News*, 69, 171). We should therefore expect the same proportion of loss in pig iron and steel analysis, or about 0.006 per cent. silicon in a 0.20 per cent. silicon steel, and about 0.10 per cent. in a 3 per cent. silicon pig iron.

² The liquid boiled down rapidly in a capacious covered casserole (evaporating dishes do not serve) on a very hot plate.

the appearance of sulphuric fumes, and it was thought therefore that this process favored the dehydration of the silicic acid. Later it was found, however, that with one evaporation the loss of silica was usually just as great or greater than in using the regular method.

Upon experimenting with the old Swedish method reintroduced by Dr. Kinsey, and which consists in the use of sulphuric acid alone,¹ without nitric or any other acid, it was found that the silica lost by incomplete dehydration in this method was usually less than 0.006 per cent. silicon and with stirring not resorted to at all.

Drown's method, silicon lost. Per cent.	Writer's method, silicon lost. Per cent.	Swedish method, silicon lost. Per cent.
0.018	0.016	0.002
0.012	0.028	0.000
0.018	0.018	0.002
0.020	0.028	0.006
0.016	0.026	0.000
0.022	0.020	0.006
0.012	0.006
0.034	0.012
0.012	0.008
0.014
0.018	0.028	0.006
0.018	0.022	0.000
0.028	0.022	0.000
0.012	0.034	0.012
0.032	0.006
0.024	0.006
0.018	0.006
0.010	0.004
0.030	0.002
0.020

The silicon percentages in these steels ranged from 0.15 to 0.25. Silicon lost in each case was determined by evaporating the filtrate. All evaporation were to dense fumes. The Swedish method seems to be in use in but a comparatively few (though large and important) laboratories, but for steel analysis deserves a wider popularity. In the case of high carbon steels the liquid in a covered dish may be boiled down rapidly on a thin steel plate, heated by a full Bunsen flame, to the end of the operation

¹ Hydrochloric acid doubtless serves as well.

without lowering the flame.¹ However the dehydration is just as complete when evaporated slowly.

The writer uses 50 cc. of dilute sulphuric acid (1 : 4) for 2.351 grams drillings steel, and observes that solution is complete before the sulphuric acid becomes concentrated. But in the determinations of silicon in steel given by Drown's method in the first table the proportion of sulphuric acid used was for part of them 10 cc. concentrated acid to 1 gram drillings and for the remainder 3.5 cc. per gram drillings. The following results from a 3.55 per cent. silicon pig iron show that in pig iron analysis as regards the point under discussion Drown's method is as effective as the old Swedish.

Drown:	silicon lost, per cent,	0.168, 0.14, 0.14, 0.164, 0.133, 0.152
Swedish	" " "	0.096, 0.096, 0.096

That these losses are due not to the iron sulphate protecting the silicic acid, but to the cause already referred to in a foot-note, is shown by the results of a number of tests made by the Swedish method and with five minutes' stirring after appearance of fumes in which the respective losses were 0.152 per cent. and 0.112 per cent. silicon; and also by another test by the Swedish method, in which two evaporation were made before filtration and in which the loss was 0.108 per cent. silicon. Incidentally it is shown by these and the above tests that the hydrofluoric acid treatment usually insisted upon should not be included in a silicon determination, unless the silica remaining in the filtrate be recovered or allowed for. The same is, of course, true also of ferrosilicons.

The following results from different ferrosilicons give some hint of the proportion these mutually opposing errors are apt to bear to each other.

The silica lost is about 3 per cent. of the total as usual. The hydrofluoric acid residues seem to be apt to run somewhat less.

Silicon lost, per cent.....	0.43, 0.23
H. F. residues, per cent.....	0.16, 0.24, 0.14

In the following table total silicon (silicon as usual plus silicon in filtrate) results by the Swedish method are compared with total silicon results by Drown's method.

¹ An impossible operation in Drown's method; impossible also, usually, in this method, in the case of low carbon steels and wrought irons. For such, it is perhaps better to use hydrochloric acid instead of sulphuric.

Steel.	Drown's method. Per cent.	Swedish method. Per cent.
A	0.190	0.190
"	0.190	0.196
"	0.196
"	0.192
B	0.178	0.184
"	0.178	0.182
"	0.182
"	0.190
C	0.204	0.202
"	0.202	0.204
"	0.202	0.200

LABORATORY OF HENRY DISSTON & SONS'
STEEL WORKS, PHILADELPHIA.

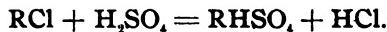
ON THE DECOMPOSITION OF THE CHLORIDES OF ALKALI METALS.

By C. W. VOLNEY.

Received February 23, 1901.

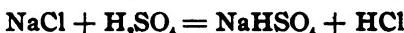
PART I.

THE action of sulphuric acid on the chlorides of the alkali metals is usually expressed by



It has been observed that concentrated sulphuric acid acts with considerable violence on the alkaline chlorides at the common temperature ; that an acid, which has been diluted with one-quarter or one-third of its weight of water, acts with less violence, developing hydrochloric acid gas on the application of heat ; and it is known that, if less acid than as above is used, the hydrochloric acid gas is developed only on applying considerable heat. Thus we observe that in the manufacture of sulphate by the Leblanc process, 2 molecules of salt are used with 1 molecule of sulphuric acid (60° Bé) and that, whereas, only about 70 per cent. of the hydrochloric acid gas is driven off in the pans, the mass has further to be calcined at a high temperature in the calcining furnaces, to complete the decomposition. We have, therefore, *a priori* to conclude that, in order to effect a thorough decomposition of the chloride by sulphuric acid, the application of heat is necessary ; that the decomposition takes place periodically, as the temperature is raised, and that it is generally presumed that

the entire decomposition is effected at a lower temperature when the materials are used in quantities corresponding with



than with



But it may be stated here that the operation does not take place quite in accord with this theory. If we bring concentrated sulphuric acid in contact with sodium chloride at the common temperature, the action takes place at once; the mass foams under development of hydrochloric acid gas, and ultimately ceases. When the quantities used correspond with the bisulphate formulation, a considerable portion of the gas is driven out, but hardly one-half of the theoretical quantity. If the mass is not heated, the process is ended, so that even with sufficient acid to form the bisulphate, only about one-half of the chloride is decomposed; the other half can be decomposed only by the application of heat.

For the purpose of investigating this matter, I undertook first to determine the quantity of hydrochloric acid gas, which is developed during the indicated phases of the process.

I effected the decomposition of the chlorides in an apparatus very much like those usually described for the preparation of hydrochloric acid. As the mass foams very much, when concentrated acid is used, the flask is of ample proportion and provided with a thermometer, safety funnel, and gas delivery tube. Between the absorption vessel and the development flask I inserted an empty bottle with safety tube, serving as receiver of substances carried over from the flask, and also as a safety valve.

At each phase I drew through the apparatus a sufficient quantity of air, to carry the gas from the apparatus into the absorbing water. An aliquot portion of the solution of hydrochloric acid gas in water served for the determination of hydrochloric acid by normal soda solution. In this process, equivalent proportions of the chlorides and sulphuric acid in grams were used.

The temperatures in the flask during the periods of gas development were noted.

I. DECOMPOSITION OF SODIUM CHLORIDE.

To 117 grams sodium chloride, 200 grams sulphuric acid (sp. gr. 1.84) were added.

The evolution of gas is violent; the mass foams. Temperature,

18°. No rise of temperature is observed. In the absorption vessel was a liter of water, of which, after the reactions were finished, aliquot portions (100 cc.) were used for the determination of hydrochloric acid.

It was found that the flask, containing the salt and sulphuric acid, should be frequently shaken to effect the reaction, otherwise only an imperfect decomposition of the chloride takes place. This is shown by the following two series of determinations, one resulting from the flask left at rest, and the other frequently shaken. From 117 grams sodium chloride, one-half of the theoretical quantity of HCl (73), that is, 36.5 grams, should be set free and found in the absorbing water:

Percentages found.	
I.	II.
26.49	33.58
25.91	32.12
27.61	34.31
26.50	33.58
26.50	34.42
27.31	33.60
26.00	34.12
....	34.30
Average 26.6	33.7

Theoretical amount, 36.5.

This shows that 95 per cent. of the theoretical amount of hydrochloric acid has been developed; and that only 46 per cent. of the total amount of the acid has been set free at the common temperature by an excess of sulphuric acid.

The residue in the flask solidifies almost entirely to a salt cake, when left for a length of time undisturbed. Shortly after the gas development ceases, it shows a mixture of an oily liquid with undecomposed sodium chloride, and in the liquid, needles of crystallization begin to form. If at this time the liquid is poured off from the forming salt cake and filtered, crystals are obtained, which show the composition NaH_2SO_4 , and as it appears somewhat difficult to effect a separation of these crystals from the remaining sodium chloride and free sulphuric acid, I will describe an improvement on the filtering apparatus, which I have used on former occasions for similar purposes.¹ The bell-jar was connected with a Woulfe bottle containing sulphuric acid in such

¹ This Journal, 23, 490.

a way as to admit dry air to the jar through a tube with stop-cock.

The liquid or salt mixture is poured on a platinum cone, which is finely perforated, and placed into the funnel of the filtering apparatus, which is placed into the bell-jar. When the air is exhausted, the faucet is opened sufficiently to let a very slow stream of air pass through the apparatus. This air is dried by sulphuric acid. By means of this filtration in a vacuum, the superfluous sulphuric acid is removed from the crystals on the platinum cone, and, as I have found by comparative tests, the salt on the filter may be washed with concentrated sulphuric acid to remove any traces of sodium chloride, without changing the crystallization on the filter. This is owing to the fact that the polysulphates, formed in the salt cake of the flask, are not affected by concentrated sulphuric acid. In this manner material for analysis was obtained, and the parts of the salt crystallizing from sulphuric acid, or from the oily liquid in the flask before solidifying, gave, on analysis, the following results:

	I.	Found.	III.	Average.	Theory for $\text{NaH}_3(\text{SO}_4)_2$.
Na.....	9.31	8.100	8.70	10.550
H ₃	2.11	11.8	1.6	1.85 ¹	1.376
SO ₄	87.50	89.9	92.3	89.9	88.073
	98.92	101.7	102.00	100.45	99.999

The irregularities in these results the writer can ascribe only to the difficulty in separating the different salts, which necessarily exist in the mixture. From the foregoing, I conclude that the action of concentrated sulphuric acid on sodium chloride at 18° can be expressed thus:

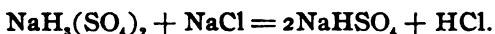


This reaction takes place without any development of heat, and with its termination the development of hydrochloric acid gas ceases.

The second period of the development of the gas commences when heat is applied to the mass. From the fact that gas develops as soon as the flask becomes warm, and that the salt cake in the flask melts easily, and the gas development continues until the cake becomes hard and dry, the reaction may be considered

¹ Omitting II.

as taking place between the polysulphate and the remaining sodium chloride and may be expressed thus:



The mass in the flask showed, at the end of this part of the process, nearly 120° . The salt cake is now the usual bisulphate. The hydrochloric acid gas absorbed in the same manner as described in the first part of the process, measured by titration with normal alkali, corresponds within from 2 to 7 per cent. in excess with the calculation. This great difference is evidently owing to the fact that quantities of the sodium chloride escape contact with the sulphuric acid, in the measure, as the salt cake becomes thick or solid. The difficulties in the practical manipulation in this investigation consist mainly in the impossibility, so far, of separating the trihydrogen sodium disulphate from the remaining sodium chloride, or from any other sulphates, which may be formed during the first period or phase of the action of the sulphuric acid on the chloride. On contact with atmospheric air, water is very quickly absorbed by the liquid and also by the polysulphates, and the result is then always sodium bisulphate and diluted sulphuric acid.

2. DECOMPOSITION OF POTASSIUM AND AMMONIUM CHLORIDES.

In the continuation of the experimental part of this investigation, the action of concentrated sulphuric acid on potassium chloride and ammonium chloride, during the first phase of the reaction, has been examined. The quantities brought in contact at the common temperature, 17° - 18° , complied with $\text{RCl} + \text{H}_2\text{SO}_4$. The temperature of the mixture of potassium chloride and acid remains stationary until the acid has come well in contact with the chloride, when the temperature rises from 17° to 30° , receding again to 17° after the corresponding reaction is finished. When sulphuric acid reacts on ammonium chloride under the same conditions, the temperature falls quickly from 18° to 1° .

This work is to be continued.

Reference to Literature :

Carl Schultz: "Ueber saure Salze der Schwefelsäure," Pogg. Ann., 1868.

QUANTITATIVE DETERMINATION OF FLUORINE IN FLUORIDES EASILY DECOMPOSABLE BY SULPHURIC ACID.¹

By W. R. BURK.

Received September 3, 1901.

In determining the purity of commercial fluorite, two methods were found outlined which appealed as practicable, one described by Hillebrand,² based upon the method of Rose, and the one of M. Carnot described at length in a paper "Sur le dosage du fluor."³

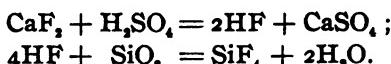
A modification of Carnot's method, as recommended by Cairns, was tried but with little success.

The method described by Hillebrand, while satisfactory for complex silicates, was not found as suitable as that of Carnot, and a modification of the latter with certain precautionary additions was adopted with satisfactory results. Without these additional precautions, however, the method does not give accurate results, but invariably shows too high percentage of fluorine.

The method adopted is as follows :

A perfectly dry mixture of about 3 grams of dry powdered and calcined silicon dioxide and 0.20 gram of dry powdered fluorite with 40 cc. concentrated sulphuric acid is digested at a temperature of 120° to 135°, the silicon tetrafluoride evolved being conducted through a perfectly dry conducting tube to a narrow upright vessel containing about 20 cc. of a freshly prepared 10 per cent. solution of potassium fluoride. The end of the conducting tube dips into a sufficient pool of pure mercury to prevent moisture from entering the tube. A slow current of dry air is passed while the temperature of the sulphuric acid mixture is maintained for one and a half hours.

The reactions involved are as follows :



In the receiving vessel :



The potassium fluosilicate separates out partially, and after

¹ This paper is an extract from a portion of a thesis presented to the Rose Polytechnic Institute for the Master's degree.

² Bulletin 176 of U. S. Geological Survey.

³ Compt. rend., 114; 750 (1892).

transferring to a subsiding vessel and adding an equal volume of 90 per cent. alcohol it subsides perfectly to a heavy pulpy stratum. After a half hour the contents are filtered, using a Gooch crucible with asbestos plate, washed free from potassium fluoride with 90 per cent. alcohol and dried to constant weight at a temperature of 100° C. Two-thirds of the fluorine of the potassium fluosilicate comes from the fluorite, or the weight of the salt, multiplied by the factor 0.34511, gives fluorine; and this multiplied by 2.0527 gives the calcium fluoride.

The detail manipulation must be followed with great care, in which case only will satisfactory results be obtained. The three chief sources of error are :

1. Moisture in air current or conducting tubes, resulting in premature decomposition of the silicon tetrafluoride in the tubes and even clogging of the tubes.

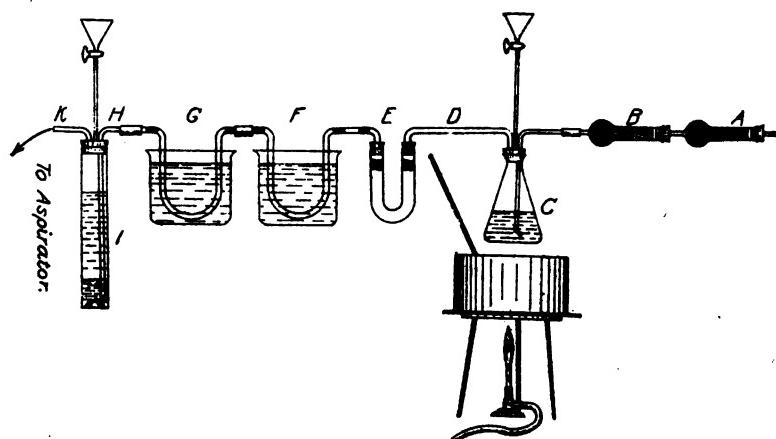
2. Sulphuric acid fumes carried over by a current of air, resulting in the decomposition of the potassium fluoride of the solution in the receiving vessel and the formation of potassium fluosilicate with consequent high percentage determination.

3. Flakes of insoluble addition products of potassium fluoride of the solution with silicon dioxide of the walls of the glass (where used) receiving vessel. A 10 per cent. solution of potassium fluoride attacks glass quite readily and high percentage is usual from this source unless great care is taken.

These sources of error are so serious that early in the experimental work, while using a sample of rather pure fluorite, containing 98.77 per cent. calcium fluoride, values as high as in one case 130 per cent. calcium fluoride, and in another 113 per cent. calcium fluoride were obtained.

Details of the method are as follows, in which statements and references are made to the accompanying sketch of apparatus :

Tube *A* contains glass wool saturated with concentrated sulphuric acid and tube *B* contains fused calcium chloride. From these drying tubes a conducting glass tube extends to the bottom of vessel *C*, which is an Erlenmeyer flask of 150 cc. capacity, closed with a three-holed rubber stopper, the second and third holes of which are closed with a stop-cock funnel and a glass tube *D*, one end of which terminates just below the rubber stopper, the other end of the tube projecting into a U-tube, *E*, plugged at points indicated by cross hatching with pure glass wool. *F* and *G* are



U-loops bent from 5 mm. glass tubing, connected with tight rubber joints and plugged with glass wool at the points indicated, the plugs being designed to interrupt the current of air and effect a stoppage of sulphuric acid fumes which are not otherwise eliminated. *H* is a glass tube extending to the bottom of the vessel *I*, and terminating in a contracted end bent upward. Into the containing vessel *I* is placed sufficient pure dry mercury to seal the opening of the tube *H* by 2 mm. to 3 mm. at least. Vessel *I* is closed with a three-holed rubber stopper, through which a stopcock funnel, and the tube *K* enter.

Tube *K* leads to an aspirator. The conducting tubing from *C* to *H* measures in length some 2 meters and contains in all 7 plugs of glass wool. Each part of the apparatus is dried by warming and exhausting the air before the apparatus is set up. After the apparatus is adjusted, a current of air is allowed to pass while the parts are again heated with a naked flame. The current of air is now stopped and about 20 cc. of a freshly prepared solution of potassium fluoride (10 per cent.) are poured into the vessel *I* by means of a funnel.

Three grams of pure powdered silicon dioxide are calcined and, while still slightly warm, are intimately mixed in an agate mortar with 0.20 gram of the fluorite, which has been powdered and thoroughly dried. This mixture is transferred to the flask *C* and the same immediately closed. Forty cc. concentrated sulphuric acid are now added through the stop-cock funnel. This acid, before

use, should be aerated with a current of dry air while being heated to a temperature of about 165° C.

The flask containing the mixture is now heated in an oil-bath at a temperature of 120° for one and one-half hours, during which time a current of air is allowed to pass at a rate such that bubbles in the vessel *I* can be easily counted. Flask *C* is also shaken vigorously occasionally in order that bubbles of the froth-like scum may be broken. The U-tubes are immersed in beakers filled with cold water. At the end of the operation the stopper, with connections, is removed from the vessel *I*, and the *H* tube rinsed with a little water.

The solution above mercury is removed by means of a bulb pipette and rubber mouth tube, and transferred to a small subsiding beaker. The vessel *I* is then rinsed gently with water and the mercury washed. As little water is used in washing as possible, the solution and rinsings being kept down within 75 cc. A thin, somewhat tenacious coating on the inner wall of the vessel *I* should not be removed, as this is due to addition-products of the potassium fluoride of solution with the glass. Care is also taken that no minute globules of mercury are transferred to the beaker. An equal volume of 90 per cent. alcohol is now added and the beaker allowed to stand to perfect subsidence. Decant and filter through a Gooch filter with reduced pressure. The subsiding vessel should be rinsed well though not rubbed. A tared crucible with asbestos plate is used, and after filtering, the contents are washed with 90 per cent. alcohol till the filtrate gives no turbidity with barium chloride. The crucible and contents are now dried at 100° C. in a hot air oven to constant weight, and fluorine or calcium fluoride estimated.

M. Moissan, in a paper on his investigations of fluorine,¹ mentions the decided tendency of fluorine and its simple compounds to form addition-products. This action, constituting the third chief source of error above mentioned, could be best eliminated by the use of platinum for the vessel *I*, and with this substitution the method would be very satisfactory. Platinum could be used with equal satisfaction and much economy of time for the conducting tubes from vessel *C* to vessel *I*.

The modification of Carnot's method as proposed by Cairns consists in using potassium chloride instead of potassium fluoride,

¹ Annual report of the Smithsonian Institution for 1897.

and catching any escaping hydrochloric acid gas in a connected wash-bottle. The contents of the two vessels are then titrated with standard alkali solution. The objection to this method is that the end of the titration reaction is very indefinite and indeterminate, due to a secondary reaction. (See "Grundlinien der anorganischen Chemie," Ostwald, pp. 433-436.)

THE REDUCTION, IN AN ALKALINE SOLUTION, OF 2,4,5-TRIMETHYLBENZALAZINE AND THE PREPARATION OF SOME DERIVATIVES OF THE REDUCTION PRODUCTS.

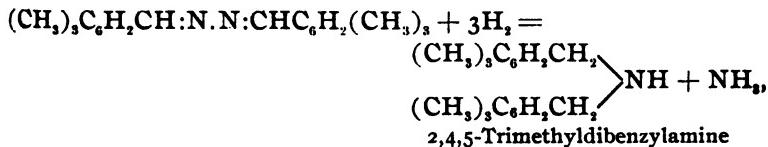
BY EVERHART PERCY HARDING.

Received September 9, 1901.

THE experimental part of this paper was carried out in the chemical laboratory at the University of Heidelberg under the supervision of Prof. Curtius, and a short abstract of it has already been published in the July, 1900, number of the *Journal für praktische Chemie*.

The formation of azines by the condensation of aromatic aldehydes with hydrazine and their reduction in an acid or alkaline solution is a comparatively new line of work and the investigation along this line has largely been done by Prof. Curtius and his students at the University of Heidelberg.

2,4,5-Trimethylbenzalazine, $(\text{CH}_3)_3\text{C}_6\text{H}_2\text{CH}:\text{N.N:CHC}_6\text{H}_2(\text{CH}_3)_3$, yields different reduction products, the kind depending upon the quality of the reducing agent used and the degree of the reduction. Curtius and Franzen,¹ by reducing in an acid solution, using zinc dust and acetic acid, obtained 2,4,5-trimethyldibenzylamine, a solid substance melting at 78° and insoluble in water. The reaction may be represented by the equation

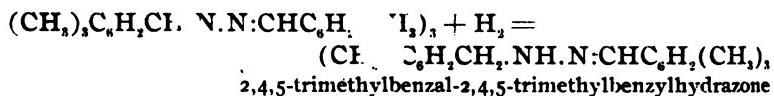


part of the nitrogen being reduced to ammonia.

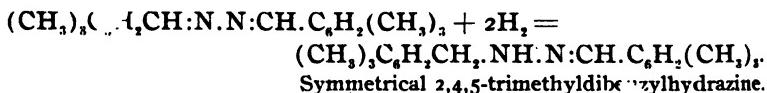
By reducing 2,4,5-trimethylbenzalazine in an alkaline solution, using sodium amalgam as a reducing agent, two reduction prod-

¹ *Ber. d. chem. Ges.*, 4, 1901.

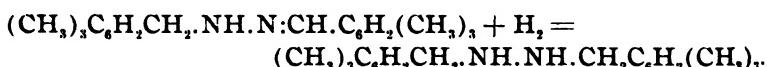
ucts were obtained, the kind depending upon the degree of reduction — one a 2,4,5-trimethylbenzal-2,4,5-trimethylbenzylhydrazone, $(CH_3)_3C_6H_2CH_2NH.N:CHC_6H_2(CH_3)_3$, produced by a partial reduction, the other a symmetrical 2,4,5-trimethyldibenzylhydrazine, $(CH_3)_3C_6H_2CH_2NH.NH.NH.CH_2C_6H_2(CH_3)_3$, produced by a complete reduction. The reactions may be represented by the following equations:



and



The symmetrical hydrazine may be obtained also from the hydrazone by a further reduction.



Each of these reduction products is a solid substance and comparatively unstable.

The azines are aliphatic compounds, derivatives of the hypothetical azimethylene —CH.N.N.CH—, and by a partial reduction one would expect a symmetrical reduction product—either a hydrazymethylene derivative, =CH.NH.NH.CH=, in which the valence of nitrogen has changed from III to V or an azomethane derivative corresponding to the aromatic azo compounds and having the general formula R—CH₂N:N.CH₂—R. But this is not the case as is evidenced by the decomposition products which show an unsymmetrical reduction, the compounds having the general formula R—CH₂NH.N:CH—R. By hydrolyzing the hydrazones with dilute hydrochloric acid they form an aldehyde and a substituted hydrazine, which reaction is best explained by the hydrazone or unsymmetrical formula

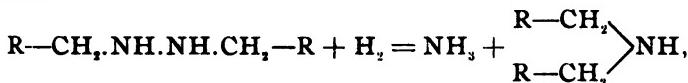


The formation of but one acetyl or benzoyl derivative favors the presence of but one imide group or one methylene group as exist in the unsymmetrical hydrazone while the two imide groups in the assumed hydrazymethylene derivative or the two methylene

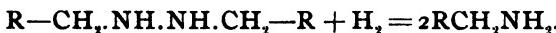
groups in the assumed azimethane derivatives would make a diacetyl or dibenzoyl derivative probable.

The symmetrical hydrazines produced by a complete reduction of the azines in an alkaline solution are also aliphatic compounds, derivatives of hydrazomethane, $R-\text{CH}_2\text{NH.NH.CH}_2-R$, which correspond to the aromatic hydrazo compounds $R-\text{NH.NH}-R$. The latter are easily reduced to primary amines while the former are stable in an alkaline solution. No attempt has been made to reduce the symmetrical hydrazine in an acid solution but the probability is that in the preparation of

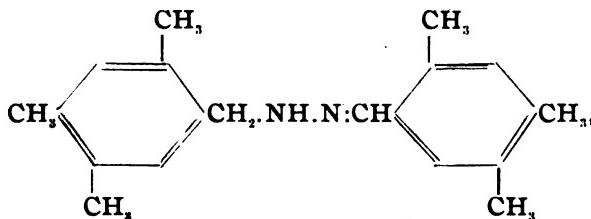
$\text{R}-\text{CH}_2\text{NH}$,
the secondary amines $\text{R}-\text{CH}_2\text{NH}$, by the reduction of the
azines in an acid solution, the symmetrical hydrazine forms as an intermediate product and then reduces further to one molecule of ammonia and one molecule of a secondary amine instead of to two molecules of a primary amine as do the aromatic hydrazo compounds, the final reaction taking place according to the equation



instead of the equation



To make 2,4,5-trimethylbenzal-2,4,5-trimethylbenzylhydrazone,



10 grams of 2,4,5-trimethylbenzalazine were placed in a round bottomed flask, of 1 liter capacity, which was provided with a reflux condenser. This was dissolved in 700 cc. of 95 per cent. alcohol by boiling vigorously on a water-bath. To the solution which was kept at the boiling-point of the alcohol there was added, intermittently, aliquot parts of 300 grams of sodium amalgam, more than a sufficient amount to reduce the azine to the hydrazone. After an interval of four hours the amalgam had

become spent and the solution nearly colorless, maintaining a slight turbidity. The mercury and impurities were filtered off and the filtrate placed in a refrigerator. In twelve hours' time 4 grams of a flaky, white, crystalline substance had separated out, which was filtered off and well washed with water. From a dilute alcoholic solution, needle-like crystals formed, while from a concentrated alcoholic solution the crystals grouped themselves in the form of tufts which melted at 134°.

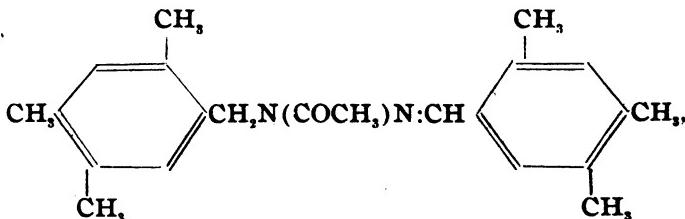
An analysis gave :

	Theoretical. Per cent.	Found. Per cent.
Carbon	81.63	81.85
Hydrogen.....	8.57	8.84
Nitrogen	9.36	9.53

The molecular weight, determined by the depression of the freezing-point method, was found to be 311 and 309.7 as against 294 the theoretical molecular weight. The hydrazone is very soluble in ether and ligroin, less soluble in alcohol and acetic acid, and insoluble in water. On exposure to the air it soon decomposes, assuming a yellow color and emitting an odor of pseudocumylaldehyde. It is unstable in an exhausted desiccator and is readily decomposed by the action of steam or hydrochloric acid.

The replaceable imide hydrogen atom makes substitution products possible. The acetylbenzoyl and nitroso groups form the corresponding stable and characteristic compounds.

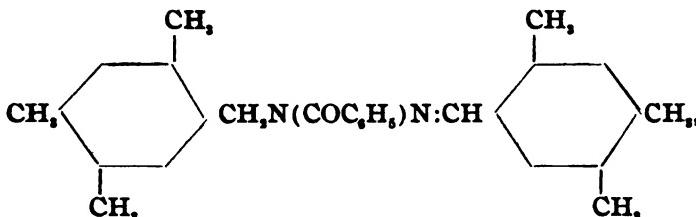
2,4,5-T trimethylbenzalacetyl-2,4,5-trimethylbenzylhydrazone,



was formed by treating a concentrated and hot alcoholic solution of the hydrazone with an excess of acetic anhydride and the excess evaporated off on a water-bath. Recrystallized from alcohol the long fine needles melted at 184°. An analysis gave :

	Theoretical. Per cent.	Found. Per cent.
Carbon	78.57	78.50
Hydrogen.....	8.33	8.36
Nitrogen	8.34	8.54
Oxygen	4.76	4.60

It is soluble in the organic solvents and insoluble in water.
The benzoyl derivative,



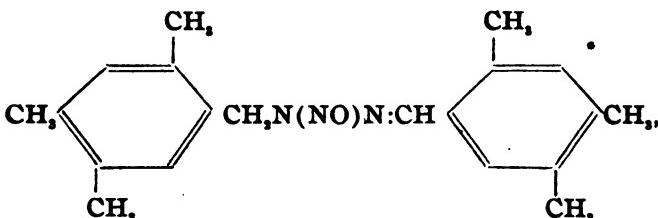
2,4,5-Trimethylbenzalbenzoyl-2,4,5-trimethylbenzylhydrazone.

was easily prepared by the Schotten-Baumann reaction. An analysis gave :

	Theoretical. Per cent.	Found. Per cent.
Carbon	81.41	81.48
Hydrogen.....	7.54	8.11
Nitrogen	7.03	6.89
Oxygen	4.02	3.52

It crystallizes from alcohol in fine needle-like crystals which melt at 187° . It is soluble in the organic solvents and insoluble in water.

The nitroso derivative,



2,4,5-Trimethylbenzalnitroso-2,4,5-trimethylbenzylhydrazone.

was prepared by adding to an ice-cold mixture of alcohol and hydrazone, concentrated hydrochloric acid, drop by drop, until the hydrazone dissolves. An ice-cold concentrated solution of sodium nitrite was then gradually added. A yellow crystalline substance separated at once, which increased upon the addition of water to the solution. The precipitate was filtered off and

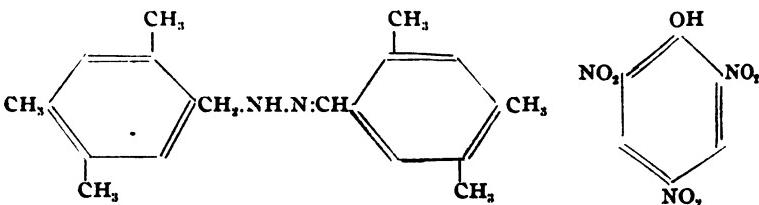
well washed with water to remove excess of sodium nitrite. Recrystallized from alcohol, the yellow needles melted at 118°.

An analysis gave :

	Theoretical. Per cent.	Found. Per cent.
Carbon	74.31	74.13
Hydrogen.....	7.74	8.27
Nitrogen	13.00	13.28
Oxygen	4.95	3.32

The nitroso derivative is soluble in the organic solvents and insoluble in water. It decomposes with concentrated sulphuric acid assuming a red color which disappears upon the addition of water and emits at the same time an odor of aldehyde. By treating an alcoholic solution of the nitroso compound with dried hydrochloric acid gas and placing the partially evaporated alcoholic solution in a refrigerator, crystals separated which melted at 155°-156°. This compound appeared to be a hydrochloride of the nitrosohydrazone, for by treating it with sodium hydroxide it formed the hydrazone melting at 134° and by treating with sodium nitrite it formed again the nitroso compound melting at 118°. In preparing the nitroso compound, the temperature must be kept near the freezing-point or the derivative will decompose.

The hydrazone is a weak base. With dilute organic acids it forms addition products, the molecule remaining intact at the double bond. With picric acid it forms a hydrazone picrate.



2,4,5-Trimethylbenzal-2,4,5-trimethylbenzylpicrate.

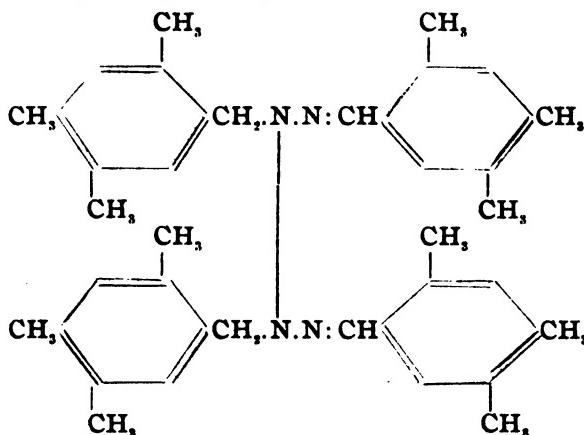
The picrate is formed by adding a concentrated alcoholic solution of picric acid to an alcoholic solution of freshly prepared hydrazone. Upon the addition of water a yellow flaky precipitate formed, which crystallized from ether in yellow needles which melted at 169°. An analysis gave :

	Theoretical. Per cent.	Found. Per cent.
Carbon	59.66	59.73
Hydrogen.....	5.54	5.16
Nitrogen	13.39	13.52
Oxygen	21.41	21.59

The picrate is insoluble in water and difficultly soluble in the organic solvents.

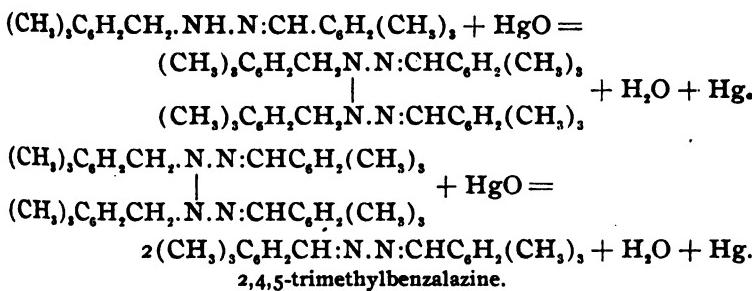
Curtius and his students' succeeded in preparing from benzal-benzylhydrazone, 4-methylbenzal-4-methylbenzylhydrazone and 2,4-dimethylbenzal-2,4-dimethylbenzylhydrazone, respectively, the corresponding tetrazones, by oxidizing with mercuric oxide.

2,4,5-Trimethylbenzal-2,4,5-trimethylbenzylhydrazone failed to give a corresponding tetrazone.

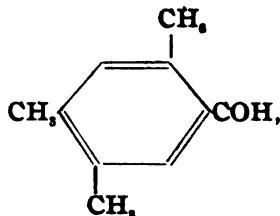


2,4,5-Trimethylbenzal-2,4,5-trimethylbenzyltetrazone.

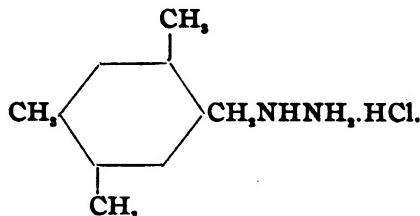
Several trials were made modifying the method of the foregoing investigator but either the unchanged hydrazone remained or 2,4,5-trimethylbenzalazine was formed. It is assumed that the tetrazone may have formed as an intermediate product which oxidized at once to the azine according to the following equations:



By the action of dilute hydrochloric acid the hydrazone hydrolyzes into 2,4,5-trimethylbenzaldehyde.



and 2,4,5-trimethylbenzalhydrazine hydrochloride,

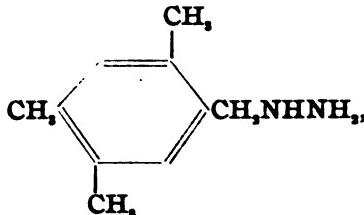


In preparing the hydrazine hydrochloride, 4 grams of the hydrazone were treated in a round-bottomed flask with 150 cc. of water and 10 cc. of dilute hydrochloric acid. Steam was then conducted through the solution; an oil-like substance distilled over which had the odor of pseudocumyl aldehyde and which formed a condensation product with hydrazine hydrate that melted at 180°, the melting-point of 2,4,5-trimethylbenzalazine. The hot residue in the flask was filtered and the filtrate distilled in a vacuum. The residue, recrystallized from alcohol, melted at 240°. An analysis gave:

	Theoretical. Per cent.	Found. Per cent.
Carbon	59.85	59.78
Hydrogen.....	8.51	8.47
Nitrogen.....	14.11	13.97
Chlorine.....	17.60	17.71

The hydrochloride is a very stable compound. It is soluble in water and insoluble in ether.

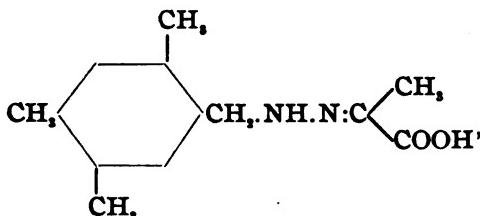
The free base 2,4,5-trimethylbenzylhydrazine,



was prepared from the hydrochloride by the action of caustic potash. Four grams of the hydrochloride and an excess of caustic potash were placed into an Erlenmeyer flask. A few drops of water were added and subsequently 50 cc. of ether. The flask was provided with a soda-lime tube to protect the base from the moisture and carbon dioxide of the atmosphere. The flask was shaken at times so as to bring the hydrochloride in contact with the potash. After twenty-four hours the ether was separated from the water layer and dried with fused caustic potash. The ether was then evaporated and the residue distilled in a vacuum. At 25 mm. pressure the base distilled over at 165° as a colorless oil, which solidified upon cooling. It is very unstable, decomposing at once when exposed to the air. An analysis gave 16.89 per cent. nitrogen as against 17.08 theoretical per cent. Upon standing three days in a desiccator, an analysis gave but 5.8 per cent. nitrogen. It began to melt at 78°, and at 85° there began a rapid evolution of nitrogen.

The base forms, with benzaldehyde benzal-2,4,5-trimethylbenzylhydrazone, a very unstable compound which melts at 89°–90°, and which dissolves in the organic solvents. It was formed by adding benzaldehyde to the free base and then rubbing the walls of the beaker with a glass rod. It was purified by crystallizing from alcohol.

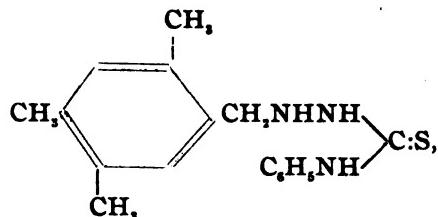
With pyroracemic acid the base forms 2,4,5-trimethylbenzylhydrazonepyroracemate,



a white crystallized substance which melted at 92°. It was prepared by adding an excess of pyroracemic acid to the hydrochloride of the base. An oil immediately formed which settled to the bottom of the flask and then crystallized. An analysis gave 11.79 per cent. of nitrogen as against 11.97 theoretical per cent. It is soluble in water and the organic solvents.

The base, 2,4,5-trimethylbenzylhydrazine, forms addition

products. With phenyl mustard oil it forms 2,4,5-trimethylbenzylphenylthiosemicarbazide,

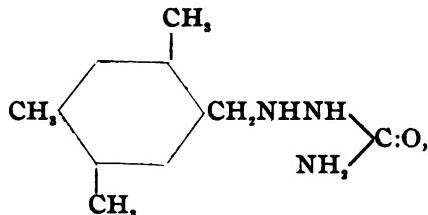


white hair-like crystals which melt at 167°–168°. It was prepared by adding to an alkaline solution of the base an excess of phenyl mustard oil, and then warming the solution. By warming at too high a temperature or with an excess of alkali the thiosemicarbazide decomposed and a black lustrous crystalline substance formed. An analysis gave:

	Theoretical.	Found.	
	L.	II.	
Nitrogen	14.09	14.42	14.22

It is soluble in ethyl alcohol, methyl alcohol, ether, benzene, and acetic acid. It is difficultly soluble in ligroin and water.

With hydrocyanic acid, the base forms 2,4,5-trimethylbenzylsemicarbazide,

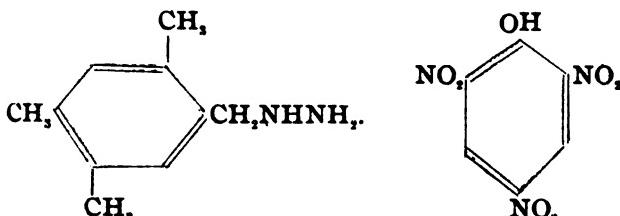


white needle-like crystals which melt at 174°–175°. It was prepared by adding to the hydrochloride a solution of potassium cyanate and crystallizing from alcohol. An analysis gave:

	Theoretical. Per cent.	Found. Per cent.
Nitrogen	20.29	20.47

It is easily soluble in ethyl alcohol, methyl alcohol, acetic acid, and benzene. It is difficultly soluble in water and insoluble in ether and ligroin.

With picric acid 2,4,5-trimethylbenzylhydrazine forms 2,4,5-trimethylbenzylhydrazine picrate.

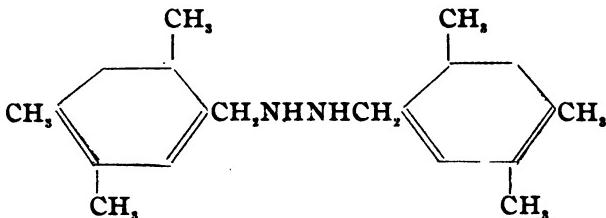


This addition product crystallizes in yellow needles which melt at 163° . In its preparation an ether solution of picric acid was gradually added to a water solution of the hydrochloride. The picrate formed at once as yellow crystals at the contact point of the two layers. By adding an ether solution of picric acid to a warm solution of the hydrochloride, the picrate formed as an oil, which settled to the bottom of the flask and subsequently crystallized. An analysis gave:

	Theoretical. Per cent.	Found. Per cent.
Nitrogen	17.81	17.64

It is difficultly soluble in warm water and insoluble in ligroin and benzene.

Preparation of symmetrical 2,4,5-trimethyldibenzylhydrazine,



As has previously been given, 2,4,5-trimethylbenzal-2,4,5-trimethylbenzylhydrazone was formed by a partial reduction of 2,4,5-trimethylbenzalazine. By a further reduction of the hydrazone or a stronger reduction of the azine solution the symmetrical 2,4,5-trimethyldibenzylhydrazone was formed. In the preparation of this compound 10 grams of 2,4,5-trimethylbenzalazine were dissolved in 500 cc. of 95 per cent. alcohol. To this warm solution in a round-bottomed flask provided with a reflux condenser was added, at times, aliquot parts of 300 grams of a 4 per cent. sodium amalgam. The solution was kept on a water-bath at the boiling-point of the alcohol for six hours dur-

ing which time the amalgam was added. The mercury and impurities were filtered off and the filtrate cooled in a refrigerator. Two grams of the hydrazone separated out. This was filtered off and the cold filtrate treated with cold concentrated hydrochloric acid. A voluminous precipitate formed which increased by the addition of water. This was rapidly filtered off, washed well with water and its dilute alcoholic solution treated with sodium hydroxide. A voluminous precipitate formed which, when recrystallized from alcohol, melted at 128°. An analysis gave:

	Theoretical. Per cent.	Found. Per cent.
Nitrogen	9.46	9.47

The molecular weight by the depression of the freezing-point method gave:

	Theoretical.	Found.	
	I.	II.	
Mol. wt.	296	305.7	321

The free base cannot be obtained directly from the filtrate from the hydrazone. By evaporating the filtrate, the dibenzylhydrazine is oxidized to the hydrazone and by the addition of water to the filtrate the hydrazine decomposes. It is very unstable. It soon becomes a yellowish white, emitting an odor of 2,4,5-trimethylbenzaldehyde.

The molecular weights and melting-points of the hydrazone and dibenzylhydrazine vary but little. It was by means of the hydrochloride of the dibenzylhydrazine that it was possible to distinguish between the two compounds. The hydrazone forms no hydrochloride but decomposes, yielding 2,4,5-trimethylbenzaldehyde and 2,4,5-trimethylbenzylhydrazine while the dibenzylhydrazine forms a stable and characteristic hydrochloride which melts at 171°. In an alcoholic solution it soon decomposed, and by boiling the solution almost immediately.

2,4,5-trimethylbibenzylhydrazine, as was previously given, is an aliphatic compound, a symmetrical derivative of hydrazimethane, $\text{CH}_2\text{NH} \cdot \text{NHCH}_2$, corresponding to the hydrazo compounds of the aromatic series. The aromatic hydrazo compounds oxidize very readily, the colorless hydrazobenzene oxidizing in a very short time to the red azobenzene by means of atmospheric oxygen. The corresponding aliphatic hydrazi compounds also oxidize readily but do not form the corresponding azo compounds. They form either symmetrical tetrazenes with the general formula

$=\text{N} \cdot \text{N} \cdot \text{N} \cdot \text{N} =$,¹ or oxidize first to the corresponding hydrazone and then to the unsymmetrical tetrazone with the general

formula $\begin{array}{c} | \\ -\text{N}-\text{N}^+ : \\ | \\ -\text{N}-\text{N}^- : \end{array}$, or to the azines with the general formula

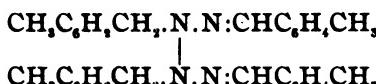
$-\text{CH} \cdot \text{N} \cdot \text{N} \cdot \text{CH}^-$.² Curtius and Franzen³ succeeded in oxidizing dibenzylhydrazine, $\text{C}_6\text{H}_5\text{CH}_2\text{NH} \cdot \text{NH} \cdot \text{CH}_2\text{C}_6\text{H}_5$, to dibenzyltetrazone and gave it the formula



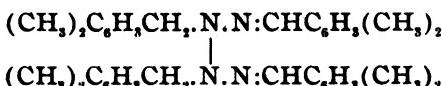
Curtius and Propfe attempted to obtain the symmetrical 4-methyldibenzyltetrazone, $(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2)_2\text{N} \cdot \text{N} \cdot \text{N} \cdot \text{N} (\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2)_2$, by oxidizing symmetrical 4-methyldibenzylhydrazine,



but succeeded in obtaining the unsymmetrical 4-methylbenzal-4-methylbenzyltetrazone,



Likewise Curtius and Haagar,⁴ in attempting to oxidize 2,4-di-methyldibenzylhydrazine, $(\text{CH}_2)_2\text{C}_6\text{H}_4\text{CH}_2\text{NH}_2\text{NHCH}_2\text{C}_6\text{H}_4(\text{CH}_2)_2$, to the symmetrical tetrazone, obtained the unsymmetrical 2,4-di-methylbenzal-2,4-dimethylbenzyltetrazone,



Neither the symmetrical nor unsymmetrical tetrazone could be isolated by oxidizing symmetrical 2,4,5-trimethyldibenzylhydrazine with mercuric oxide. Either or both of these compounds may have formed as intermediate products but the only compound that could be isolated after the oxidation was 2,4,5-trimethylbenzalazine.

Schmidt and Schulz⁵ succeeded in substituting two acetyl groups for the two imide hydrogen atoms in the aromatic hydrazobenzene, thus forming a diacetyl derivative,

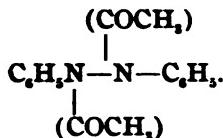
¹ *Ber. d. chem. Ges.*, 4, 1901.

² *J. prakt. Chem.*, N. F., 62, (1900).

³ *Ber. d. chem. Ges.*, (1900).

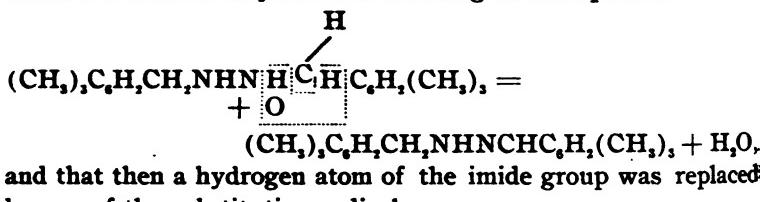
⁴ *J. prakt. Chem.*, N. F., 62, (1900).

⁵ *Ann. Chem. (Liebig)*, 207, 327.



The diacetyl, dibenzoyl, and dinitroso derivatives¹ of dibenzylhydrazine have been prepared. Also the dibenzoyl derivative² of 4-methyldibenzylhydrazine and the diacetyl derivative¹ of 2,4-dimethyldibenzylhydrazine.

None of the corresponding diderivatives of 2,4,5-trimethyldibenzylhydrazine have been prepared. In every trial a mono-derivative of 2,4,5-trimethylbenzal-2,4,5-trimethylbenzylhydrazone was formed. It is assumed that the symmetrical hydrazine was oxidized to the hydrazone according to the equation



THE PRECIPITATION OF COLLOIDS BY ELECTROLYTES

BY W. R. WHITNEY AND J. F. OBER

Received August 20, 1955

PART I

REVIEW OF THE WORK OF PREVIOUS INVESTIGATORS

THE purpose of this article is to call attention to the present condition of our knowledge concerning colloids by coordinating some of the facts and conceptions which have resulted from the work of various investigators in this field, and to append thereto a contribution to the subject, the result of recent experiments of our own together with a fairly complete index to the literature. It is hoped that the significance of this subject and its probable importance in connection with biological chemistry in its widest significance, as well as its claim to general chemical interest, may be brought more fully to the attention of chemists.

Any discussion of the subject which considers its history must begin with a reference to the work of Graham. He distinguished

¹ *J. prakt. Chem.*, N. F., **62** (1900).

a new class of substances which exhibit little or no chemical affinity, which do not crystallize, which dissolve in various solvents apparently without any limiting solubility therein, which exhibit little or no tendency to diffuse when in solution, and which may be filtered from their solutions by animal membranes or parchment. These substances also exhibit the property of gelatinization or coagulation, the change often being spontaneous or brought about or catalyzed simply by the presence of acids, salts, etc. Graham gave the name colloid to this class of substances and called their solutions in water, alcohol, etc., hydrosols, alcrosols, etc., while the names hydrogel, algogel, etc., were given to the coagulum. He recognized that both organic and inorganic substances existed in these forms, and there were thus classified together such chemically different materials as silicic acid, ferric hydroxide, and gelatine.

The application by van't Hoff of the laws of gases to dissolved substances, together with Arrhenius' theory of dissociation, has shown us the probable molecular condition of many substances in solution. It has thus become often only necessary to determine the electrical conductivity of a solution, its freezing- or boiling-point, its vapor-pressure, or one of a number of other properties, to learn whether the solute is present as simple molecules, or as polymerized or dissociated molecules. The extent of this association or dissociation may also be calculated.

A large part of the recent literature on the subject of colloids is concerned with attempts to learn the condition of the dissolved substance by some of the methods referred to. This work may be briefly summarized by stating that in most cases the conditions under which the measurements were made only left open the alternative conclusions that there was no substance in solution in the sense that ordinary acids, bases and salts and many simple organic substances dissolve, or the dissolved substance was possessed of an exceedingly high molecular weight corresponding to an association or polymerization not easily understood.

Thus Sabanejew (30)¹ by means of freezing-point determinations is forced to attribute a molecular weight of over 100,000 to silicic acid in the hydrosol, while experiments by Gladstone and Hibbert (27) similarly lead to the conclusion that the molecular weights of ferric hydroxide and aluminum hydroxide in solution

¹ Such figures refer to the references at the end of this article.

exceed 5,000. It may be true that molecules of such magnitude exist in solution and that to them may be ascribed all the functions of simple dissolved molecules, but in the absence of proof that such is the case it will probably be more fruitful to follow the plan of several modern investigators (116, 49, 35,), and consider the colloid solutions as simple suspensions of otherwise insoluble material. With this in view the first step is naturally to compare so-called colloidal solutions with what are known to be simple suspensions or heterogeneous mixtures. If a hydrosol resembles a mixture of sand and water in which the sand, because of its degree of fineness, does not settle, then the two ought to have other common properties. Such is actually the case, and it may be truly said that the hydrosols possess only those properties which would naturally be ascribed to them if they were regarded as suspensions of finely divided insoluble substances.

It would be impracticable here to consider in detail the hundreds of different colloids thus far studied, but a cursory view of the methods of their production will call attention to the following general principle : when any substance is produced within a liquid in which it is insoluble, it will, at least temporarily, exist there in the so-called colloidal state ; but this colloidal state is rapidly destroyed by the presence of electrolytes.

A clearer idea of the value of what follows will be gained if one recognizes at this point the probable necessity of attributing electrostatic charges to particles of any kind when suspended in a liquid, and of assuming that these charges, while they may be positive or negative for different kinds of suspended matter, must still be of the same sign for all particles of the same substance. It is known that two different substances in contact assume equal and opposite electrostatic charges at their contact surfaces, and the work of Quincke, Coehn, and others has brought to light the regularities of this phenomenon.

Suspended particles of finely divided sulphur, silica, etc., in water, exhibit negative charges exactly as larger masses of the same substance in contact with water do, and when the suspension is placed between two electrodes connected with a source of electromotive force, the particles all migrate in the direction of the negative current. Conversely too, water in capillary tubes made of such materials as charge themselves negatively in contact with it, moves with the positive electricity through the capillary

under the influence of the electric current. Similarly, particles suspended in turpentine assume in most cases the opposite charge as compared with the water, and under influence of the electric current move in the opposite direction.

Coehn (99) was led to conclude that a substance having a higher dielectric constant than the liquid in which it is suspended assumes the positive charge, while if of lower dielectric constant its charge is negative. It is probable that this does not alone determine the nature of the charge, which at least in many cases must depend also on electrolytic solution pressure and the partition coefficient for the ions of dissolved electrolyte between the suspended material and the liquid (123).

We seem forced then to recognize electrostatic charges on suspended particles, and it seems just as necessary to accept the conclusion that, as a result of these charges, suspended particles, whose masses are small enough, are equally distributed throughout the liquid and prevented from ever coalescing or settling because of the mutual repulsion of these charges. This mutual repulsion might also cause measurable osmose and corresponding osmotic pressure, properties which the colloids have to a slight degree.

The following illustrates some of the relations between "sols" and suspensions, the various methods of producing colloidal solutions or hydrosols, and the fact that absence of electrolytes usually insures permanency of colloidal state.

If an aqueous solution of a silicate be treated with the equivalent quantity of an acid, free silicic acid and a salt are formed. This silicic acid is in the colloidal state, not in the form of a simple dissolved substance, and if the salt present is not very dilute, the acid becomes coagulated or exhibits its insolubility; *i. e.*, the particles of suspended acid collect together. If the electrolyte be removed by osmose or otherwise, or if the silicic acid be made by such a method that electrolytes do not remain in the solution, the hydrosol is stable. It may, however, be precipitated at any time by the addition of electrolytes. For example, stable silicic acid hydrosol may be made by treating silicon tetraethyl with water, the alcohol resulting not having any effect on the silicic acid. This remains in the "sol" condition indefinitely but is precipitated by any electrolyte (Grimaux 16). Bredig (83) has shown that a great many metals may be produced in the hydrosol state by simply

forming an electric arc under water between terminals of the metal desired. The heat of the arc volatilizes the metal and the vapors condense in the water, yielding deeply colored suspensions or colloidal solutions which often do not settle in measurable time, but which are immediately precipitated by even traces of most electrolytes and are not affected by non-electrolytes.

If arsenic or antimony sulphide be produced by the action of hydrogen sulphide on aqueous solutions of the oxides of these metals, there is at no time any considerable concentration of electrolytes present and there always results a deeply colored liquid, from which nothing is separated by ordinary filtration. Linder and Picton have studied these hydrosols and have shown that very low concentration of electrolytes completely precipitate them. Most other insoluble sulphides have been produced in the hydrosol state and have shown the same properties (Winninger 26).

Sulphur in the hydrosol state may also be produced by the mutual action of aqueous solutions of sulphur dioxide and hydrogen sulphide. The sulphur thus formed in the absence of electrolytes is in a stable, apparently soluble condition, from which it is precipitated by the presence of electrolytes (Stingl and Morawsky 12). Selenium also undergoes the same modification by analogous treatment (Schulze 19).

The hydroxides of many of the metals may be made as hydrosols by methods which involve the principle above stated. A solution of ferric hydroxide in aqueous ferric chloride solution, when subjected to osmose to remove most of the chloride, yields a colloidal hydroxide solution which is stable, but is precipitated by most electrolytes. Grimaux (16) has shown that by the reaction between ferric ethylate and an excess of water, stable ferric hydroxide hydrosol is produced. Here there are no electrolytes present like those which, in the usual metathetical reaction for the production of such compounds, cause a coagulation and precipitation of the insoluble substance. Other hydroxide hydrosols may be made in a similar manner.

A solution of one part of egg albumen in ten or more parts of pure water does not yield any visible insoluble matter on boiling, although the effect of the heat may well have produced the insoluble material which more concentrated albumen solution would yield when similarly treated. This solution of so-called

modified or alkali albumen is capable of coagulation or precipitation by electrolytes, although it is stable in their absence (Hardy 131, 132).

Several purely organic colloids have been synthetically produced by Grimaux (16) and by Pickering (69), but always in the absence of electrolytes; moreover electrolytes easily precipitate or coagulate them, while non-electrolytes do not. There are produced in nature, in growing plant and animal cells, many colloids which probably owe their precipitation or deposition to electrolytes; this fact makes the study of the properties of this class of bodies of the utmost importance to biology.

In the case of simple, well recognized suspensions of insoluble material, such as silica, clay, oil, etc., it has long been recognized that the settling or coagulation is produced or very greatly accelerated by electrolytes, while non-electrolytes have little or no effect. This principle is used in connection with stamp-mills, etc., for the precipitation of so-called slimes, and it is of interest to the geologist in that it accounts for the formation of the delta at a river's mouth, where the settling seems to be induced by salt water rather than by loss of current in the stream. It is a principle also applied in the purification of water supplies and sewage. It has been studied by Scheerer (3), Barus and Schneider (35), Spring (139), Stark (114), and many others.

In general, acids and the salts of heavy metals are most active in this coagulative effect on suspensions, the alkali salts having the power to a less marked degree, but the general property of electrolytes of precipitating such suspensions, even when the former is exceedingly dilute, is repeatedly discovered. Similarly, as shown in the methods of preparation, the hydrosols or colloidal solutions are capable of coagulation or precipitation by electrolytes and often by exceedingly minute quantities. The colloidal platinum described by Bredig (83) is often precipitated in a few hours by the impurities in ordinary distilled water, while in very pure water it is stable for months or years. Quantitative work on this precipitation will be described later. It may be said here, however, that in this respect there seems to be really no difference between ordinary suspensions and so-called hydrosols. The two classes, if indeed they are not identical, also have the common property of very slight diffusibility and of behaving alike when filtered through porous cells (133), parchment membranes, etc..

and they practically, without exception, exhibit in a pencil of light the Tyndall phenomenon of diffusion of the ray. Its path through the liquid is visible and the reflected light of the ray is polarized.

Several investigators, among them Linder and Picton (80), Coehn (79), Spring (112), and Hardy (131), have shown that the colloidal material, in the hydrosol or so-called dissolved condition, migrates under the influence of the electric current and collects about one electrode, the direction of movement depending on the nature of the colloid. This is exactly what Quincke (5) and others have observed for visible particles in suspension under the same conditions.

Thus it seems most logical to consider so-called colloidal solutions as finely divided suspensions, the particles of which are much larger than simple molecules, the mixture being heterogeneous, instead of homogeneous, or consisting of two phases instead of one. This point has been very recently briefly discussed and a theory proposed by Donnan (147).

A number of investigators (Schulze, Linder and Picton, Hardy) have studied quantitatively the precipitation of the colloids by electrolytes, and very interesting results have been obtained. At least in the case of many of the colloids, the molecular concentration of the acid or salt required to produce coagulation is determined almost wholly by the valence of the positive ion, being independent of the nature of the negative ion and having nearly the same value for different positive ions of the same valence. The reciprocal of this concentration is designated the coagulating power of the electrolyte; and if its value for positive univalent ions be represented by 1, that of the bivalent ions becomes about 30 and that of the trivalent about 1000. Quantitative experiments by four different chemists on the sulphides of arsenic, antimony, and cadmium, on the hydroxide of manganese, and on boiled dilute egg albumen, have shown the above ratio to hold fairly well. This point may well be illustrated by examples: Colloidal antimony sulphide is precipitated by most of the univalent salts when the concentration is about 1 part by weight of salt to 200 parts of the solution; for the bivalent salts, this value is about 1 part by weight to 2,000 of water, while with the trivalent ions, 1 part of the salt to 30,000 or 40,000 of water is sufficient. Corresponding concentrations

of non-electrolytes are practically without effect. Another author states that sodium, potassium, and ammonium salts precipitate colloidal copper sulphide when 1 part by weight of the salt is present in from 60 to 400 parts by weight of water. Salts of the bivalent elements, when present, 1 part in from 3,000 to 7,000 parts of water and the trivalent salts in from 30,000 to 70,000 parts of water. Undissociated acids are without effect, while dissociated acids are about like univalent salts. For a certain arsenious sulphide solution, 1 part of potassium chloride to 137 parts of water is necessary; while with ferrous sulphate and similar salts, 1 part in 2000 or 3000 parts of water, and with ferric chloride 1 part in 50,000 parts of water suffices, the values for iron, chromium and aluminum in this case being 50,000, 83,000 and 20,000. As might be expected, the alums here act as trivalent-metal salts, while the ferrocyanide and ferricyanide of potassium act like other valent-metal salts. Experiments on suspended sulphur by one author, and on diluted, boiled egg albumen by another, have shown the same quantitative relations.

Several chemists have suggested possible explanations of these phenomena. It is thought by some recent investigators that the coagulating power of salts on aqueous suspensions and on many of the so-called colloids, is attributable to the positive or to the negative ion of the salt, depending on whether the suspended particles themselves are negatively or positively charged with respect to the solution; that is, that the negatively charged suspensions are precipitated by positively charged ions, and conversely. Spring (139) believes the statical charge, which it is assumed the ions of electrolytes carry, neutralizes the statical charges of opposite sign on colloidal particles, and cites cases which seem to support the belief. For example, he states that certain colloids are negative and therefore require for their immediate precipitation or coagulation a certain concentration of a positive ion. Solutions of various salts of the same cation should therefore be equally active as precipitants when they are equivalent in concentration, while equivalent solutions of salts of the same anion should not be equally active. This he has shown to be the case. Whetham (121) has attempted to explain the observed relative coagulating or precipitating powers of ions is influenced by their valences as follows. He assumes that it is necessary that a certain

minimum electric charge, carried by the ions, must be brought within reach of the colloidal group with a certain minimum frequency throughout the solution in order to produce coagulation. Evidently equal charges should be available from $2n$ triad ions, $3n$ diads and $6n$ monads, where n is a whole number. Probability of contact between colloid and ion should be proportional to the concentration C of the ion or equal to AC , where A is a constant. The probability of two such ions being together is \overline{AC}^2 and of " n " ions \overline{AC}^n . For equal coagulative power of ions of different valences $\overline{AC}_1^{2n} = \overline{AC}_2^{3n} = \overline{AC}_3^{6n} = B$ (a constant). The concentration of trivalent, bivalent and univalent ions respectively being C_3 , C_2 , C_1 , hence $C_1 : C_2 : C_3 = 1 : B : B^{1/2} = 1 : K : K^2$, where K is a constant. That is, from the known coagulating powers of univalent and bivalent ions, that of ions of higher valencies could be calculated. The calculated and observed values for trivalent ions thus far investigated agree very satisfactorily. Measurements with quadrivalent ions have not been made.

Whetham supposes a certain minimum charge has to be brought into contact with the colloid particles with a certain minimum frequency throughout the solution. We see no reason for assuming a certain minimum frequency. On the contrary it is more probable that whenever contact between any colloid particle and a certain necessary minimum amount of electric charge takes place, coagulation of that particle results, and that the frequency of contact simply determines the rapidity of coagulation of the solution as a whole. Evidently then, we might have various concentrations of the same electrolyte, all of which precipitated the colloid completely, but after expiration of different times. This velocity would then be a function of the concentration and for immediate precipitation the relationships might hold, as shown by Whetham. It is a well-known fact that with all the colloids the velocity of coagulation or precipitation may assume any desired magnitude depending on the concentration of precipitating agent. The many comparisons of the coagulating power of different electrolytes for immediate coagulation led to the discovery probably first stated by Schulze, but confirmed by Linder and Picton and others, that ions of the same valence have only approximately the same precipitating or coagulating power, while for different valence the

power is greatly different as stated above. Spring has added the velocity of migration of the ion as a factor in determining its precipitating power because of the fact observed by him that potassium, sodium, and hydrogen in this respect stand in the order of their migration rates. Such a dependence is to be expected if the assumption of Whetham is a correct one. In this connection it is interesting to note that Linder and Picton have observed, apparently, a peculiar class of analogous phenomena in the case of colloidal aniline colors. They mixed solutions of aniline colors which migrate in opposite direction under the influence of the current and whose particles under our present hypothesis are possessed of opposite electric charges, and report that "in general there is a tendency to aggregation between such substances." The mixed solution was either completely precipitated or the particles simply increased in size; just such effects as are produced by electrolytes in large and small quantities respectively. Thus, aniline blue (—) and methyl violet (+) mix in this way, and, unless very dilute, precipitate; and even when dilute, optical tests show that the particles have increased in size. Aniline blue (—) and magdala red (+) give similar results. In dilute solutions, to show that some union had taken place, the authors filtered the mixture through a porous cell, which held back both in case of the mixture, while aniline blue would filter through when tested separately. Rosaniline hydrochloride and aniline blue acted similarly. Here, as Linder and Picton state, we have what appears to be "a mimicry of the ionic dissociation," but is there any reason why it may not be a true conception of the actually occurring phenomena?

Finally, it must be mentioned that Linder and Picton have stated that when a colloidal solution, or, as they designate it, a pseudo solution, of arsenious sulphide, is precipitated by a salt such as barium chloride, a small portion of the barium is precipitated along with the sulphide, while the corresponding quantity of the negative element, chlorine, is not, and that this barium cannot be removed from the precipitate by washing with water. It can, however, be replaced by another positive ion by washing with a solution of an appropriate salt.

PART II.

EXPERIMENTS ON THE CO-PRECIPITATION OF THE ELECTROLYTE
WITH THE COLLOID.

The results of Liunder and Picton, which have just been referred to, seemed to us to open a field of great scientific interest, and one likely to become of much practical importance to the analyst, in connection with the carrying down and retaining of otherwise soluble materials by precipitates. In order to confirm and extend these results, our investigation was undertaken. A colloidal arsenious sulphide solution was made by pouring a solution of Merck's C. P. arsenious oxide, a little at a time, into an excess of a saturated aqueous solution of hydrogen sulphide, so that the resulting solution contained about 1 per cent. arsenious sulphide. The excess of hydrogen sulphide was then removed by passing washed hydrogen through the mixture. There resulted a deep lemon-yellow solution which was opaque by reflected light but transparent by transmitted light, and which, except for a practically unweighable quantity of precipitated sulphide, passed readily through the best filter-paper. It also showed no signs of heterogeneity under the microscope. The water used in these experiments was twice distilled, the second time from alkaline permanganate solution, and was such as is usually employed in electrical conductivity measurements. An approximately 1 per cent. solution of barium chloride was made by dissolving the crystallized salt in water. Thirty cc. of this solution were added to 200 cc. of the colloidal solution, which produced immediate and complete precipitation of the arsenious sulphide. This was filtered and carefully washed until the washings gave no test for chlorine with silver nitrate. The barium in the filtrate and wash-water was then precipitated as sulphate and weighed, and at the same time a determination of the barium in 30 cc. of the original barium chloride solution used was likewise made. The weights of sulphate obtained were 0.2590 and 0.2849 gram respectively, which correspond to 0.1523 and 0.1675 gram of barium; or a loss of 0.0152 gram of barium which was held by the precipitated sulphide. The analysis of the filtrate from the arsenious sulphide precipitate for chlorine by weighing silver chloride showed 0.0863 gram as compared with 0.0865 gram found in the same way in 30 cc. of the barium chloride solution used.

This shows that the chlorine was not carried down with the sulphide to a measurable extent.

To determine the effect of concentration of the colloid on this phenomenon, half as much, or 100 cc., was taken and diluted to 200 cc., the volume used above. Thirty cubic centimeters of the barium chloride solution as before were added to this and the analysis made as above. It was found that 0.0078 gram of barium had been carried down by the sulphide. Finally 100 cc. of the colloid solution, 80 cc. of water, and 50 cc. of the barium chloride were mixed and the process carried out as before. The barium held by the sulphide was here 0.0075 gram. As these are practically half of the previous quantity (0.0152), it is evident that *the composition of the precipitated colloid is independent both of its own concentration in the solution and of that of the barium ions.* The approximate relationship in the precipitate is represented by the symbol $90(\text{As}_3\text{S}_3) : \text{Ba}$. It is doubtless true that the barium exists here as hydroxide as will be shown below. That the barium remained adhering to the sulphide, was shown by the following experiment, which is a repetition of Linder and Picton's procedure. 100 cc. of the colloid solution were diluted with 100 cc. of water and coagulated with 30 cc. of the barium chloride solution. The precipitate was washed free from chloride and then allowed to stand in dilute ammonium chloride solution for two days. The precipitate was again filtered and the barium in the ammonium chloride solution determined as sulphate. Thus 0.0071 gram of barium was found, which was 93 per cent. of that carried down by the sulphide (0.0076 gram). This had been removed from the washed sulphide by the ammonium chloride solution. This is in accord with Linder and Picton's statement that the metal carried down by the arsenious sulphide can be replaced by other metals by digesting as above.

The natural assumption to make in the light of these experiments is that the colloid causes hydrolysis of the salt and that while the base is carried down in the precipitate, the filtrate contains the free acid. How this precipitation of a basic hydroxide can be produced, together with the liberation of the acid, is yet to be explained. That the filtrate in the above experiments did contain free acid after the process, while it did not before, was readily shown, and the quantity which was found by titration with alkali agreed with the assumption. For example,

in cases where, as above, 200 and 100 cc. of the colloid had been used, the free acid in the filtrate was found to be equivalent to 0.0081 and 0.0038 gram of chlorine respectively. The very dilute solutions made the determination difficult; but these values correspond quite well with the results in the case of the barium carried down which require 0.0079 and 0.0039 gram respectively. Therefore, *equivalent quantities of barium and hydroxyl are precipitated with the colloid.*

This power of what one might consider chemically inert material, by virtue of which it decomposes neutral salts in the presence of water and combines with or holds either the acid or base, has already been discovered in the case of solid substances, especially porous material such as bone-black, silica, precipitated colloids, and has received very interesting treatment by Van Bemmelen (141). In the case of solids, however, quantitative measurements seem hardly destined to lead to such interesting results as are promised by a study of what appears to be the same phenomenon in colloidal solutions.

The experiments above described have been repeated, using strontium, calcium, and potassium chlorides instead of barium chloride, and the following results which are tabulated below, together with those given above, were obtained. The calcium was precipitated as oxalate and weighed as oxide. The strontium was weighed as carbonate and the potassium as potassium platinichloride. In the first column is given the amount of the colloidal solution used, in the second the quantity of water added, in the third the volume of the precipitant used, in the fourth the weight of the metal in the precipitant used, in the fifth the weight of this metal carried down by the precipitate, in the sixth the weight of chlorine found in the filtrate as free acid, and in the seventh the weight of chlorine corresponding to the metal in the fifth column.

CALCIUM CHLORIDE.

Colloid solution. cc.	Water. cc.	Precipitant. cc.	Metal in solution. Gram.	Metal in precipitate. Gram.	Chlorine as free acid. Gram.	Chlorine calculated from metal. Gram.
100	100	25	0.0724	0.0020	0.0036	0.0036
200	...	25	0.0724	0.0038	0.0073	0.0067
100	100	25	0.0724	0.0041	0.0036

STRONTIUM CHLORIDE.

200	...	25	0.1071	0.0072
200	...	25	0.1071	0.0083
100	100	25	0.1071	0.0040

BARIUM CHLORIDE.

Colloid solution. cc.	Water. cc.	Precipitant. cc.	Metal in solution. Gram.	Metal in precipitate. Gram.	Chlorine as free acid. Gram.	Chlorine calculated from metal. Gram.
200	...	30	0.1675	0.0152	0.0081	0.0079
100	100	30	0.1675	0.0078	0.0038	0.0039
100	80	50	0.2791	0.0075

POTASSIUM CHLORIDE.

100	2.0	0.0032	0.0030	0.0029
200	5.0	0.0073

The quantities of these various metals carried down by 100 cc. of the colloid are calculated and collected in the following table. The third column contains the quantities of the respective elements chemically equivalent to the barium absorbed. This element is chosen on which to base a comparison, because its quantitative determination is probably the most accurate.

I.	II. Grams observed.	III. Grams calculated.
Ca	{ 0.0019 { 0.0020	0.0022
Sr	{ 0.0036 { 0.0041	0.0049
Ba	0.0076	0.0076
K	0.0036	0.0043

In the case of another solution of the colloid which contained 19 grams of arsenic trisulphide per liter, the following results were obtained :

Colloid solution. cc.	25 cc. chlo- ride solution.	Metal in solution. Gram.	Chlorine as acid. Gram.
50	Ba	0.1394	0.0019
50	Ba	0.1394	0.0021
50	Ca	0.0706
50	Ca	0.0706
50	Ca	0.0706	0.0017
50	Sr	0.1071	0.0021
50	K	2.00	0.0021
100	Ba	0.1394	0.0039
100	Ba	0.1394	0.0039
100	Sr	0.1071	0.0042
100	Ca	0.0706	0.0041
100	Ca	0.0706	0.0040
100	K	2.00	0.0038

The determinations of the quantity of metal carried down by the precipitate were not made in these experiments as the time at our disposal would not permit it. The analysis of the filtrate for free acid was considered a measure of the quantity of metal car-

ried down by the precipitate as it proved itself to be in the previous experiments where both were determined.

Therefore, since the quantities of free acid were found to be the same, within the limits of error, in all the experiments, it is evident that equivalent quantities of the four metals were precipitated with the colloid. Thus, not only does this colloid, when precipitated, bring about a hydrolysis of the salts, absorb the base, and liberate the acid, but, what is equally striking, it carries down with itself chemically equivalent quantities of the different bases. In other words, *into this precipitated colloid, barium, strontium, calcium, and potassium enter in the proportions of their equivalent weights.* It is evident that this result supports the hypothesis of Whetham (see above).

PART III.

AN INDEX TO THE LITERATURE OF COLLOIDS.

The accompanying list of references is a fairly complete one and includes some articles which are only indirectly connected with the subject. To facilitate its use, the matter treated in the article is briefly stated, we having taken the liberty of substituting in many cases descriptive clauses for the titles given the papers by the respective authors. Owing to the necessary brevity of these modified descriptions, much very important material contained in many of the articles is still not specially referred to, but it was thought that even these brief descriptions might facilitate the use of this collected literature.

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NOTE.

Reply to Dr. Ewell's "Notes on the Paper by Hiltner and Thatcher."—In an article recently published in this Journal, we outlined a modification of the Sachs-Le Docte modification of Pellet's "instantaneous aqueous diffusion methods for the estimation of the sugar content of beets." In the succeeding number of the Journal, Dr. E. E. Ewell published some notes on our paper¹ criticizing the proposed modification in several points. Inasmuch as Dr. Ewell has apparently fallen into some of the errors which we specifically warned against in our previous article, it would seem that a further word of comment is necessary. This reply has been delayed by the withdrawal of Mr. Thatcher from this laboratory and by the many distractions of the summer vacation season, but may not be out of place at this time.

¹ This Journal, 23, 432.

The object for which the work reported in our previous article was undertaken, was an investigation of the possibility and feasibility of doing away with the necessity of weighing an exact definite weight of beet pulp for each analysis, and using instead any known weight of pulp with its proportionate amount of water and lead subacetate solution. When we began the work we were unaware that such a device had ever been suggested, since Walawski's work had not yet been published in any of the journals on file in our library. Subsequent correspondence with the Division of Chemistry at Washington, secured for us a copy of a translation of the paper of Dr. Sachs from which we quoted freely in our article. After we had completed our work and a copy of the report of it had gone into the hands of the printer, a personal letter from Dr. G. L. Spencer informed us that he had for some time past been making use of a modification of the method in question, by which any desired weight of pulp might be proportionately diluted, clarified, and polarized. The idea, although original with ourselves, was therefore not new, but inasmuch as our modification differed in some essentials from the commonly adopted methods, and in some important respects from Walawski's process, particularly as to practical details—its publication was considered advisable.

Dr. Ewell criticizes the suggested modification because it is based upon a correction for the volume of water in the beet rather than the volume of juice, or liquid in the beet. It is admitted at the outset, of course, that either the Sachs-Le Docte assumption of an average juice factor or our assumption of an average water factor will give results varying somewhat from the truth in individual cases. Which of these two assumptions is the more desirable as a basis for a rapid method for technical analysis depends, therefore, upon two things : first, the probable error that may be introduced in individual analysis, and, second, the ease with which a factor to accurately represent the average of the beet to be analyzed may be determined.

Researches during the past ten years by sugar-house and experiment-station chemists show that the amount of *marc*, or insoluble matter, in the beet often rises to 8 per cent. and sometimes even to 10 per cent. of the weight of the beet. A very large number of direct determinations of this factor made at this laboratory during the past seven years shows that in immature or

low-grade beets, it sometimes falls as low as 2 per cent. This is shown in the following table:

TABLE I. INSOLUBLE MATTER (MARC) IN BEETS.

Year.	Number of determination.	Maximum. Per cent.	Minimum. Per cent.	Average. Per cent.
1892	15	8.4	2.5	4.1
1894	6	4.6	2.2	3.3
1895	14	7.0	2.4	3.7
1896	7	3.6	2.0	2.4
1897	10	5.9	2.2	3.5
1898	8	4.0	2.0	2.9

Hence the assumption of 5 per cent. of insoluble solids, or 95 per cent. of juice, as an average for the calculation of the volume occupied by this juice must produce a significant error in many cases. The tediousness and extreme difficulty of a direct determination of the amount of insoluble matter in beets, and the unreliability of the results obtained by an indirect estimation of this factor, make it almost impossible to control the work of any given season or portion of a season by a determination of the correct average juice factor of the beets to be analyzed.

Furthermore, the calculation of the volume occupied by a definite weight of juice by the ordinary methods is subject to several errors. In the first place the usual method of determining the specific gravity of the juice by means of the Brix spindle gives erroneous results because the spindle is calibrated in solutions of pure sugar. Investigations carried on in this laboratory through several seasons show that the results obtained in this way are almost invariably too high, the percentage of total solids obtained by a direct determination, or indicated by an accurate determination of the specific gravity of the juice, being always less than that indicated by the spindle. As is shown in the following table, the real coefficient of purity is always higher than that obtained by calculation from the Brix spindle and polariscope readings. In other words, the amount of non-sugars in solution is less than that generally accepted and the volume of the resulting solution is, therefore, less.

TABLE II. REAL VERSUS APPARENT PURITY.

Year.	Number of determinations.	Differences between real and apparent purity.		
		Maximum difference. Per cent.	Minimum difference. Per cent.	Average difference. Per cent.
1892	13	+ 9.10	+ 3.30	+ 6.2
1894	6	+ 6.30	+ 3.30	+ 4.6
1895	15	+ 9.13	+ 2.96	+ 5.2
1896	10	+ 5.97	+ 1.20	+ 3.4
1897	14	+ 5.97	+ 2.34	+ 3.8
1898	9	+ 4.80	+ 1.70	+ 3.3

It is evident, then, that the only correct basis from which to calculate the volume of any given weight of juice is a direct determination of the specific gravity of the juice, or of the total solids in solution in it. This latter is the same determination upon which we base our correction for water content.

Again, even though the volume of the juice in the sample taken be correctly determined, the figures are of no real value in determining the volume of water to be added, since the juice is clarified by the same process by which its volume is to be increased to the *normal* dilution, the percentage of solids in solution being materially diminished with its attendant effect upon the volume of the solution. A portion of the soluble non-sugars as well as a portion of the lead in the clarifying agent are removed from the solution by precipitation. The exact amount of the diminution in volume due to this cause in any particular case it is impossible to determine. It is obvious, however, that Dr. Ewell's carefully prepared tables, based upon the assumption that the juice in the pulp taken has the same specific gravity as would a solution which contained a percentage of pure sugar, equal to the apparent amount of total solids in the juice, and that the solution contains all the solids originally present in its constituents are not true to facts and lead to erroneous conclusions. Moreover, both of the errors introduced are such as would, in actual practice, tend to diminish the total volume of the solution and so in part, counteract the error due to the increase in volume caused by the sugar dissolved on the water of the juice.

It would seem, therefore, that both the theoretical consideration of the matter and the practical results obtained, and reported in our previous article, show that the assumption of an average water factor as a basis for a rapid working method is fully as satisfactory as that of an average juice content. The determination of the correct average factor to be used in any series of analyses is unquestionably much more easily made in the former case. The error in individual cases might be lessened by doubling the dilution as required by the Sachs-LeDocte modification, but as was pointed out in the previous article (see page 310), this has not been found necessary in ordinary work.

Dr. Ewell further criticizes our work "because their determinations of the water contained in beets, * * * are higher than is indicated by previous results or determinations of the amount of

filter contained in beets" and further states "that as little as 4 per cent. of marc is possible, but 2.61 per cent. is doubtful and 2.28 per cent. is still more so" and supports his criticism by tables calculated from assumed conditions. The figures cited in Table I above are sufficient to show that the results recorded are not at all impossible, but, on the contrary accord very satisfactorily with the other observed facts concerning the beets with which we had to deal. The results which we have recorded on pages 308 and 309 in every case were those obtained by the best of the direct methods of determination and not by indirect calculations using arbitrary factors. It is but fair to add that, owing to very late warm Fall rains in Nebraska last year, the beets which were available for work at that time were very largely immature and unripe ones. It is hoped that in the near future, the applicability of the proposed method may be further tested on a better class of beets. The determinations of moisture recorded on page 309 of the original article were made on beets at all stages of growth from samples taken from July 15th to November 15th of each year, and, hence, as was stated, represent widely varying conditions of the beet.

It is a fact well known among chemists actively engaged in work with beets that the factors arbitrarily adopted to represent an average beet are often far from the real conditions to be met with in actual work and that percentages calculated from these arbitrarily assumed standards are by no means sufficiently reliable to afford a basis for criticism of results obtained in actual practice.

Our critic makes a number of logical deductions from certain computations that he has made, but we must beg to insist that he errs considerably in his premises. As a basis for his calculations on page 433 he makes an assumption as to purity coefficient (80 per cent.) which is quite untenable in view of the facts as ascertained by us. The coefficients of purity of the beets in question seldom reached 75 per cent., as our records show; many analyses indicated a purity of less than 70 per cent., some indeed as low as 65 per cent. Were we to apply such factors as these in the same manner as Mr. Ewell has applied the factor 80 we would obtain most astounding figures. The danger in building too much on averages and on conventional factors is here very apparent.

Although a little remote from the main point in question we

wish finally to notice the fact that in making these computations for the tables on page 433; errors have been made aside from those just mentioned. The values there used, for average sugar content in the beets, were obtained by us by indirect analysis of the beets. The percentages of sugar in the juices were first determined and from these the percentages in the beets were estimated by deducting the conventional 5 per cent. for marc. Using these same figures in connection with other data, Mr. Ewell *calculates* the percentages of marc to range from 1.79 per cent. to 4.74 per cent. The error also in attempting to calculate *soluble non-sugars in the beet* and later the percentage of marc by employing an assumed factor (or even a definitely determined factor) of *purity of the juice* is quite apparent. (By factor of purity of the juice we mean, of course, the ratio of sugar in the juice to soluble total solids in the juice; and by soluble non-sugars the difference between total solids and sugar in the juice.) By thus confusing the values for the beet and those for the juice it is manifestly impossible to compute values for marc or other components of the root.

To conclude, we wish only to again draw attention to the facts stated on page 311, *et seq.*, of the current volume of this journal regarding the experimental part of our work and especially to Table III. where the results obtained by the proposed method are compared with those secured by Pellet's hot aqueous diffusion process (an acknowledged standard method). The results given certainly point plainly to the reliability of the method and indicate that the process is based on correct principles.

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THE CHEMICAL ANALYSIS OF THE APPLE AND SOME OF ITS PRODUCTS.

By C. A. BROWNE, JR.

Received September 24, 1901.

In the Fall of 1899, the writer was called upon, by the Pennsylvania Department of Agriculture, to make a chemical study of the apple and its various products. The results of this investigation have been embodied in Bulletin No. 58 of the Department's publications. For the complete tabulation of all the analyses made in connection with this work, together with the discussion of the results, reference is made to the above bulletin. A brief summary of the results is presented,¹ however, in this connection, preliminary to a more complete description of the methods of analysis employed. The latter, in fact, is the main purpose of the present paper, inasmuch as no description of methods was included in the original bulletin. The methods herein described, while designed especially for the examination of apples and apple products, have been used successfully in a few other instances, and the writer believes that, with a few modifications perhaps, they could be employed in the analysis of any of our common fruits.

¹ This is done with the kind permission of Prof. John Hamilton, secretary of the Pennsylvania Department of Agriculture.

COMPOSITION OF APPLES.

	Reducing Water.	sugars.	Sucrose.	Starch.	Ash.	Acid as malic.	Marc.
Unripe apples (2 analyses)	80.67	6.43	2.84	3.92	0.27	1.14	...
Summer apples (6 analyses)	85.00	7.10	3.36	1.04 ¹	0.28	0.68
Winter apples (21 analyses)	83.16	8.16	4.16	0.26	0.59	1.85 ²

The above analyses represent simply the composition of the edible or fleshy portion of the apple. These figures, together with other determinations made upon the combined pulp and marc from different varieties of fruit, have furnished the following table:

APPROXIMATE AVERAGE COMPOSITION OF THE FLESH OF THE RIPE APPLE.

Ingredient.	Per cent.
	<i>Inorganic.</i>
Water	84.00
Ash	0.30
Sugars :	<i>Organic.</i>
Reducing sugars	8.00
Sucrose	4.00
Starch	0.00
Marc :	
Cellulose	0.90
Pentosans	0.50
Lignin	0.40
Organic acids :	
Free acid as malic	0.60
Combined acid as malic	0.20
Pectin bodies	0.40
Crude fat	0.30
Protein	0.10
Undetermined (tannin, etc.)	0.30
	100.00

THE CHEMICAL COMPOSITION OF APPLE ASH.

Ingredient.	Per cent.
Potash	55.94
Soda	0.31
Lime	4.43
Magnesia	3.78
Ferric oxide	0.95
Alumina	0.80
Chlorine	0.39
Silica	0.40
Sulphur trioxide	2.66
Phosphorus pentoxide	8.64
Carbon dioxide	21.60
	99.90
Deduct oxygen equivalent to chlorine	0.09
	99.81
Total	

¹ One analysis.² Eight analyses.

The above analysis was made upon the combined ashes from many different varieties of apples, the flesh of the fruit being the only part taken for incineration.

COMPOSITION OF APPLE JUICES.

	Specific gravity.	Solids.	Reducing sugars.	Sucrose.	Free acid as malic.	Ash.	Pectin.	Albuminoids.	Rotation Ventzke 400 mm. tube.
Juice from summer apples (5 analyses)....	1.0502	12.29	6.76	3.23	0.72	0.29	0.12 ¹	0.03 ¹	— 26.67
Juice from winter apples (4 analyses)....	1.0569	13.96	8.57	3.40	0.43	0.27	0.12 ²	0.02 ²	— 45.15

The composition of other fruit juices, from analyses made by the writer, is given for purposes of comparison.

Kind of juice.	Specific gravity.	Solids.	Reducing sugars.	Sucrose.	Free acid as malic.	Ash.	Pectin.	Albuminoids.	Rotation Ventzke 400 mm. tube.
Strawberry	1.0420	9.64	5.90	0.89	1.28	0.61	0.63	0.38	— 5.28
Red raspberry.	1.0463	11.01	5.13	2.31	1.44	0.60	0.88	0.75	+ 7.32
Black raspberry 1.0567	13.65	9.52	...	1.85	0.60	0.72	0.38	— 25.20	
Black cherry, very sweet... 1.1034	24.30	16.35	...	1.47	0.79	0.30	0.63	— 29.80	
Red cherry, sour 1.0461	11.22	7.33	...	1.32	0.57	0.25	0.56	— 12.96	

Closely related to apple juice is what is known as "second pressings", used so extensively at present for jelly-making and vinegar stock. It is made simply by wetting apple pomace with water and repressing.

COMPOSITION OF SECOND PRESSINGS.

Specific gravity.....	1.0376
Rotation Ventzke 400 mm. tube	— 31.94
	Per cent.
Solids	9.14
Reducing sugars.....	6.87
Sucrose	1.49
Ash	0.20
Undetermined (pectin, malic acid, etc.).....	0.58

The composition of completely fermented cider and vinegar is

¹ Four analyses.

² One analysis.

shown by the following figures, compiled from analyses made upon samples of known purity.

COMPOSITION OF CIDER AND CIDER VINEGAR.

	specific gravity.	Solids.	Ash.	Reducing sugars.	Acetic acid.	Malic acid.	Alcohol.	Pectin.	Albuminooids.	Rotation 400 min. tube.
Cider (6 analyses)	1.0006	2.34	0.29	0.32	0.61	0.25	5.51	0.04	0.02	— 2.34
Vinegar (4 analyses)	1.0184	2.00	0.44	0.52 ¹	6.19	0.14 none	0.17	0.01	— 2.01 ²	

COMPOSITION OF MISCELLANEOUS APPLE PRODUCTS.

	Moisture.	Reducing sugars.	Sucrose.	Ash.	Free acid as malic.	Albuminooids.	Pectin.	Marc.
Evaporated apples (2 anal.)	27.61	32.80	19.02	1.10	4.08	0.87	...	5.53
Apple butter (1 anal.)	52.58	37.20	1.14	0.97	2.52	0.25	2.15	1.14
Cider jelly (1 anal.)	44.53	49.50	2.18	1.39	3.61	...	1.60	none
Apple pomace (1 anal.)	70.76	8.09	2.40	0.49	...	1.25

METHODS OF ANALYSIS.

The methods employed in making the determinations contained in the preceding tables are in many cases simply the ordinary processes described in most books on commercial or agricultural analysis. The methods² of the official agricultural chemists were employed as far as possible. Only such departures, from the usual methods as it was found advisable to make, will be described.

¹ The writer desires at this point to call attention to a statement made by Doolittle and Hess in a recent number of this Journal (22, 219). It is said that "the solids of pure cider vinegar give no rotation with the polariscope, and little or no reducing action on Fehling's solution after the customary clarification with lead acetate." This is certainly a mistake. Of the many samples of pure cider vinegars examined by the writer at the Pennsylvania Experiment Station during the past four years, not one has failed to give a decided rotation to the left, when examined in the 400 mm. tube of the polariscope; likewise all have appreciably reduced Fehling's solution, whether previously clarified with animal charcoal or lead subacetate.

An unpublished experiment conducted by the writer at this Experiment Station shows that levulose is the only sugar present in properly fermented cider vinegar, the sucrose and dextrose having both disappeared in the course of the alcoholic fermentation. The acetic fermentation, which sets in before the last traces of levulose have been destroyed, seems to prevent the complete removal of the sugar by alcoholic fermentation, and the percentage of levulose continues, thereafter, nearly constant.

² Bulletin No. 46, revised edition, U. S. Department of Agriculture, Division of Chemistry.

Determination of Moisture and Solids.—This, apparently the most simple of all analytical processes, was found at the outset of the work to offer the greatest difficulties. The methods ordinarily prescribed recommend that the material be dried at 100° C., or even higher, until a constancy in weight is attained. In making determinations by any of these methods the writer has found it impossible to obtain any such constancy in weight; the residue would continue to lose, until its percentage became finally much less than the sum of the percentages of the different solid constituents. A decomposition of some kind was indicated and the unreliability of drying at a high temperature clearly shown.

The difficulty experienced is undoubtedly due to a breaking-up of the sugars of the fruit, principally levulose. This has been found true in the case of other bodies containing levulose, as has been shown by Carr¹ and Sanborn in their experiments upon "the dehydration of viscous organic liquids." These writers, after making "upward of 5,000 separate determinations, ranging over all the better-known methods and covering such materials as pure sugar and levulose solutions, honey, molasses, molasses 'flowers,' sorghum, beet and maize juices, etc., etc.," "conclude that it is impossible to dehydrate, quantitatively, solutions containing levulose without the occurrence of decomposition, if the temperature be 100°, the environment air, and the pressure equal to that of the atmosphere." The method finally adopted by Carr and Sanborn, to prevent this decomposition of levulose during dehydration, consists in drying the material on pumice stone in flat-bottomed dishes, at 70° C. and a vacuum of 25 inches.

The writer has been unable to find any work relating to the dehydration of fruits, or the products therefrom, *in vacuo*, but the same necessity would exist for such dehydration as with other levulose-containing materials, the presence of levulose in most fruits being sufficiently indicated by the marked levorotation, which the clarified juices give to the plane of polarized light.

In the various analyses, previously recorded, the writer effected dehydration in most cases by drying the material at 70° C. in a vacuum as recommended by Carr and Sanborn, using, however, perforated brass or copper tubes filled with asbestos for absorbing the liquid, instead of pumice stone in dishes as in the method of the above authorities.

¹ Bulletin 47, U. S. Department of Agriculture, Division of Chemistry, p. 134. See also this Journal, p. 17, (23) of proceedings.

The perforated tubes employed measured 9 cm. long by 2 cm. in diameter. In the case of liquids, fruit juices, cider, vinegar, etc., the tubes are nearly filled with freshly ignited asbestos,—the latter being tightly packed with a rod against the sides in the upper half of the tube, thus leaving a central cavity extending part way into the asbestos. Each tube thus prepared is placed into a glass-stoppered weighing-bottle of sufficient size, and the whole weighed. About 5 cc. of the liquid to be analyzed are then delivered from a pipette into the cavity in the asbestos, the object of the cavity being to secure a rapid absorption, and even distribution of the liquid through the asbestos. The weighing-bottle is then immediately stoppered and reweighed, the increase in weight being the amount of substance taken. After removing the stopper, the bottle, together with the inner tube, is conveyed to a vacuum drying apparatus, where it is dried in an upright position, at a constant temperature of 70° C. During the first few hours of the drying, a slight current of air is drawn through the vacuum compartment, in order to remove the large excess of moisture at first given off. In the last stages of the drying the air current is decreased, and the vacuum kept at about 25 inches. Eight to ten hours are generally sufficient to secure complete dehydration ; at the end of this time the weighing-bottle is removed from the oven, placed in a desiccator and, when cold, restoppered and weighed.

The bottles are then replaced in the oven and dried for a second period of a few hours to ascertain if constant weight has been secured. The first drying, however, has generally been found sufficient. A longer drying of several days has been found to produce no change in weight, when once dehydration was secured, showing that no decomposition of levulose is produced.

In determining moisture or solids in apples and other fruits the same method is employed, with the exception that the perforated tubes are filled only about one-fourth with asbestos. The grated pulp of the fruit to be analyzed is well sampled and mixed, and a small portion of 5 to 10 grams transferred through a short-necked funnel into the tube, when the bottle is restoppered and weighed. The drying is conducted as previously described ; the slight amount of liquid, which sometimes oozes out into the weighing-bottle, does no harm.

In drying fruit products of much consistency, such as jelly, it

is best to dissolve a weighed amount of the material in water, before adding to the asbestos, in order to secure a better absorption. The same necessity of drying *in vacuo* at low temperature exists with evaporated fruit products, such as dried apples. In such cases the use of the inner perforated tube is dispensed with altogether. The finely cut material is weighed out directly in the weighing-bottle and the process conducted as already described.

It might be supposed that, with fermented ciders and vinegars, owing to the disappearance of levulose during fermentation, a determination of the solids by the vacuum method at 70° C. and by drying at 100° C. in the usual way would show no decided difference. Such, however, is not the case with completely fermented ciders and vinegars; a constancy in weight is attained by drying at 100° C., but the percentage of solids is invariably less than that obtained by the vacuum method. The following is an example of this; the experiment was performed upon a pure cider vinegar.

	Per cent.	
	I.	II.
Solids by drying at 100° C., two days.....	1.48	1.50
Solids by drying at 100° C., three days	1.47	1.49
Solids by drying <i>in vacuo</i> at 70° C., two days	3.29	3.39
Solids by drying <i>in vacuo</i> at 70° C., three days....	3.28	3.39

The percentage of reducing sugar was only 0.16 per cent. so that decomposition of levulose does not explain the discrepancy. It may be due partly to the volatilization of glycerol, which is formed during the alcoholic fermentation. Indications, however, point to the presence of other substances, besides levulose, in fruit products, which are decomposable at 100° C.

The Calculation of Solids in Fruit Juices from the Specific Gravity.—The application of this principle, by means of the Brix spindle, in the analysis of juices from the beet and sugar-cane is too well known to require mentioning; it has also been applied by Kulisch¹ in the analysis of apple juices, the degrees Brix or Balling, corresponding to the specific gravity of the juice at 17.5° C., being the percentage of solids. The writer has compared this method of estimating solids with the actual determination, and the agreement has usually been very satisfactory. Instead of using degrees Brix the solids of juices may be calculated from the formula 245 ($S-1$), S being the specific gravity of the

¹ "Landwirtschaftliche Jahrbücher," 19, 110 (1890).

juice at 17.5° C. Such methods of estimating solids are, of course, only applicable in the case of fresh juices, before the beginning of the alcoholic fermentation. The following table gives the percentage of solids, as estimated and actually determined in a number of different juices.

No.	Kind of juice.	Specific gravity 17.5° C.	Degrees Brix.	Solids by formula		Actual solids at 70° C. <i>in vacuo</i> . Per cent.
				245 (S-I).	Per cent.	
1	Apple juice (second pressing)	1.0376	9.39	9.21	9.14	
2	" "	1.0474	11.73	11.61	11.36	
3	" "	1.0481	11.90	11.78	11.81	
4	" "	1.0484	11.97	11.86	11.87	
5	" "	1.0488	12.07	11.96	11.71	
6	" "	1.0517	12.75	12.67	12.78	
7	" "	1.0525	12.94	12.86	12.77	
8	" "	1.0539	13.26	13.21	13.29	
9	" "	1.0559	13.73	13.70	13.94	
10	" "	1.0560	13.76	13.72	12.83	
11	" "	1.0568	13.94	13.92	13.84	
12	" "	1.0613	14.99	15.01	14.90	
13	" "	1.0722	17.50	17.69	16.82	
14	Strawberry juice	1.0420	10.44	10.29	9.64	
15	Red raspberry juice	1.0463	11.47	11.34	11.01	
16	Black raspberry juice	1.0567	13.92	13.89	13.65	
17	Red cherry juice	1.0461	11.42	11.29	11.22	
18	Black cherry juice	1.1034	24.42	25.33	24.30	
Average			13.42	13.41	13.16	

The formula, as a rule, gives results slightly closer to the actual percentage of solids, except in case of juices of very high gravity, as No. 18 of the preceding table. The difference between actual and calculated results rarely exceeds 0.2 or 0.3 of a per cent.; there is occasionally, however, a notable discrepancy as in the case of apple juices Nos. 10 and 13. Calculating the solids from the gravity of a juice is sufficiently accurate for many purposes; such an estimation is preferable, in any case, to the old method of determining solids by drying at 100° C.

Ash.—This was determined according to the official method, about 20 grams of material being taken for analysis. In incinerating large quantities of material, to obtain ash for the ash analysis, it is necessary to exhaust the charred mass first with water. The insoluble residue is collected on a filter, burned, and this ash added to the residue left on evaporating the aqueous extract. The whole is then heated to a low redness till the ash is white.

Reducing Sugar.—This was calculated, in the various analyses given, simply as invert sugar. Strictly speaking this is not correct, for the dextrose and levulose of fruit juices are present in, by no means, equal proportions, as in apple juices where the percentage of levulose is nearly double that of dextrose. Nevertheless, when these sugars are not separately determined, it has seemed to the writer more accurate to consider the reducing sugar as invert rather than dextrose or levulose alone. The invert sugar is calculated from the weight of reduced copper according to the tables of Meissl and Wein ; such small amounts of sucrose, as are present in fruit juices, do not affect the accuracy of the determination.

In the determination of reducing sugar in fruit juices, 20 cc. of the filtered juice are measured out into a 500 cc. flask, about 300 cc. of water are added, and, after neutralizing carefully with sodium hydroxide using phenolphthalein, the volume is completed to the mark. Twenty-five cc. of this solution (1 cc. of original liquid) are taken for the copper reduction. The reduced cuprous oxide is filtered in asbestos tubes and, after drying, reduced in a current of hydrogen, and the weight of copper determined. In case of partly fermented juices larger amounts of liquid can be used for dilution. With completely fermented ciders and vinegars, which contain but very little sugar, the liquid after neutralizing needs little if any dilution. In calculating the percentage of reducing sugar, it is, of course, necessary to take into account the specific gravity of the liquid analyzed.

In determining reducing sugar in apples and other whole fruits the following method was adopted : 100 grams of the grated pulp are washed on a muslin filter in a large funnel, with repeated quantities of cold water, the filter being squeezed after each addition of water to hasten the removal of the sugar. The filtrate is caught in a 2-liter flask, and the washing continued until the liquid is nearly up to the mark. After completing the volume, the flask is shaken, and 200 cc. (10 grams of fruit) of the filtered solution are transferred to a 250 cc. flask ; this solution is neutralized with soda as before and the volume made up to 250 cc. from which 25 cc. (1 gram of fruit) are taken for the copper reduction.

The same method is used with evaporated fruit products, as with whole fruit, except that a smaller amount of material is taken for analysis. Twenty-five grams of the finely cut material

are treated with 200 cc. of water for several hours in a large beaker until the substance has swollen to a soft pulp. The material is then brought upon the muslin filter, and washed to 2 liters as before.

With fruit jellies, 10 grams of the material are dissolved in water, neutralized, and made to 1 liter.

Sucrose.—This was determined in the majority of cases from the increase in the copper-reducing power, after inversion with hydrochloric acid. In making the analysis the method of procedure is as follows :

The same amount of solution (juice, aqueous extract of fruit, etc.) is taken as in the determination of the reducing sugars; one-tenth its volume of concentrated hydrochloric acid is added, and the flask placed in a water-bath at 70° C. The contents of the flask, after reaching a temperature of 67°–70° C., are kept within this limit for exactly five minutes when the solution is cooled, neutralized, and made up to the same volume as in determining reducing sugars. Twenty-five cc. of this solution are taken for the copper reduction, the calculation being made to invert sugar as before. The difference between the percentage of invert sugar before and after inversion, multiplied by 0.95, will give the percentage of sucrose.

Sucrose has also been determined in fruit juices by means of the polariscope. 52.096 grams of juice are made to 100 cc. Fifty cc. of this solution are clarified with 5 cc. of lead subacetate, and the reading taken in the 200 mm. tube at about 20° C. The remaining 50 cc. are inverted with 5 cc. of concentrated hydrochloric acid, as described above, cooled rapidly and diluted to 100 cc. The reading is taken in the 200 mm. tube, at the same temperature as the first solution, clarifying, if necessary, with animal charcoal. The first, or direct reading increased by

$$0.1 \text{ and divided by } 2 = a, \text{ the invert reading } = b, 100 \frac{(a - b)}{142.4} =$$

percentage of sucrose, t being the temperature of the solutions at time of reading.

Levulose and Dextrose.—In many cases a separate determination of these sugars has been made. Several courses of procedure have been followed according to conditions.

In the presence of both dextrose and sucrose, the levulose was determined by the difference in polarization of the solutions at widely separated temperatures.¹ With juices, etc., the pure liquid is first clarified by means of animal charcoal, and the polariscope reading taken in a 200 mm. tube, first at about 15° C. (v) and then at about 85° C. (v'). The tube used should be provided with a metal jacket, through which water of the desired temperature is allowed to circulate. The percentage of levulose ℓ is calculated from the formula

$$\ell = \frac{v - v'}{G(t \times -0.0323)};$$

$v - v'$ = the algebraic difference between the two readings and, if levulose is present, will always be a minus quantity, owing to the fact that the rotation of levulose solutions when heated is deflected towards the right.

G = the specific gravity of the liquid.

t = the difference in temperature between the readings.

The value — 0.0323² represents the deviation (Venzke), for each degree centigrade difference in temperature, produced by 1 gram of levulose in 100 cc.

With fruit jellies, etc., a definite weight of the material (20 to 50 grams) is dissolved in 100 cc. of water and the solution, after clarifying, polarized at different temperatures as before. In this

case the percentage of levulose, or ℓ , = $\frac{100(v - v')}{W(t \times -0.0323)}$,

W being the grams of substance in 100 cc.

Knowing the percentage of levulose, and the copper-reducing power of the solution, the percentage of dextrose admits of calculation. Volumetric determinations by Soxhlet upon solutions of invert sugar have shown that for the same volume of Fehling's solution reduced, 1 part of levulose corresponds to 0.924 part of dextrose. Gravimetric determinations made by the writer upon pure solutions of invert sugar show a ratio somewhat lower than this, as the following table shows. The gravimetric method of Allihn was followed :

¹ See Wiley's "Agricultural Analysis," Vol. III, pp. 267-273.

² This figure was deduced from the general formula of Jungfleisch and Grimbert which gives the specific rotatory power of levulose for any temperature or concentration. The equation is $[\alpha]_D = -[101.38 - 0.56t + 0.108(c - 10)]$, in which t is the temperature of the solution and c the grams of levulose in 100 cc. See Landolt : "Das optische Drehungsvermögen, 2 Auflage, p. 524.

¹ Weight of sucrose taken. Gram.	² Weight of invert sugar therefrom. Gram.	³ Weight of copper. Gram.	⁴ Corresponding weight of dextrose (Allihn's table). Gram.	⁵ Ratio of dextrose to invert sugar.
0.2300	0.2421	0.4315	0.2113	1.047
0.1533	0.1614	0.2950	0.1538	1.049
0.1150	0.1211	0.2230	0.1148	1.055
0.0575	0.0605	0.1120	0.0570	1.061

It is seen that the ratio of dextrose to invert sugar increases slightly as the concentration of the solution diminishes; the variation, however, is not sufficient to make any appreciable difference in the calculations. Taking the average of the above determinations, 1 part of dextrose could correspond to 1.053 parts of invert sugar for the same weight of copper reduced. Since invert sugar is made up of equal parts of dextrose and levulose, 1 part of dextrose would correspond to 1.106 parts of levulose for the same amount of reduced copper, or 1 part of levulose would equal 0.90 part of dextrose.

Knowing the percentage of levulose the percentage of dextrose (d) may be found from the formula

$$d = D - 0.9l,$$

where D = percentage of reducing sugar as dextrose (Allihn's method), and l = percentage of levulose as found by polarization.

In the absence of sucrose the writer has calculated the percentages of dextrose and levulose from the rotation and copper-reducing power. The factors necessary to know are P , the specific rotatory power, and D , the percentage of reducing sugars as dextrose.

To determine the specific rotatory power it is necessary to know the rotation of a known amount of the sample in a tube of definite length. For this purpose in the case of fruit juices, etc., it is best to read the clarified liquid directly in a 400 mm. tube; with more concentrated products 20 grams of substance are dissolved in water and made to 100 cc. For clarification the writer has used animal charcoal in the majority of cases, though lead subacetate answers equally well and in some cases is found necessary. But very little difference has been noticed in the rotation by these two methods of clarification, provided excess of lead solution is avoided. In clarifying with lead the polariscopic reading must, of course, be corrected for the dilution. In case of a sugar polariscope with a Venzke scale, the reading must be corrected to angular degrees by multiplying by the factor 0.3468.

The formula for calculating the specific rotatory power in the case of liquids is

$$P(20^\circ \text{ C.}) = \frac{0.3468 v}{4G}.$$

v = polariscopic reading, Venzke scale, in 400 mm. tube at 20° C.

G = the specific gravity of the solution.

4 = the length of the tube in decimeters.

If the material is weighed out and made up to 100 cc. by dilution with water, the formula becomes

$$P(20^\circ \text{ C.}) = \frac{0.3468 v}{4W} \times 100,$$

W being the grams of substance taken.

The specific rotatory power of a solution being dependent upon the percentages and specific rotatory powers of its ingredients, we would have for solutions containing dextrose and levulose alone, the formula

$$53d - 90l = 100P.$$

d and l are the percentages of dextrose and levulose, and 53 and —90 are their respective specific rotatory powers, at 20° C. , the concentration for each sugar not exceeding 10 per cent.

Substituting the formula $d = D - 0.9l$ in the previous equation we obtain :

$$l = \frac{53D - 100P}{138}$$

As far as the writer has been able to compare them, these two methods of determining levulose have shown a very close agreement, as the following example, in the case of a partly fermented cider, will illustrate.

Specific gravity of cider = 1.0067 = G .

Rotation of cider at 15° C. , 200 mm. tube, Venzke scale == — $10.1^\circ = v$.

Rotation of cider at 85° C. , 200 mm. tube, Venzke scale == — $5.5^\circ = v'$.

The difference in temperature of the two readings = $70 = t$.

Substituting these values in the formula

$$l = \frac{v - v'}{G(t \times -0.0323)},$$

we find $l = 2.04$ per cent.

The percentage of reducing sugars as dextrose was $2.26 = D$.

The rotation of the cider at 20° C., 400 mm. tube, Venzke scale, $= -18.9^{\circ} = \alpha$

The specific rotatory power of the cider from the formula

$$P(20^{\circ}\text{ C.}) = \frac{0.3468 v}{4G},$$

is therefore $-1.62 = P$.

Substituting the above values for D and P in the equation

$$\alpha = \frac{53D - 100P}{138},$$

we find $\alpha = 2.04$ per cent., the same as before.

The percentage of dextrose in the cider, calculated from the formula $d = D - 0.91$, is 0.42 per cent.

Starch.—This substance has been found in all green pomaceous fruits; it no doubt occurs in other classes of fruits in the early periods of their growth, though this is a point which has not been as yet fully investigated. In the ripening of fruits the starch is gradually converted into sugar, and this process continues even after picking until no vestige of starch remains. A determination of starch is, of course, only necessary when its presence is indicated by the iodine reaction.

The estimation of starch in fruits, depending as it does upon its conversion into dextrose, offers special difficulties, owing to the large amount of reducing sugars present, and the first step in any process of analysis must consist in the removal of all the sugars before the conversion of the starch is attempted. The process usually recommended consists in washing a weighed amount of the pulp either directly upon a filter, or by decantation upon the same, until all the sugars are removed. This method of procedure has been found by the writer to be extremely tedious, owing to the large amount of washing required and to the tendency which the pectinous and gummy matters of the fruit have of clogging the filter.

The following process adopted by the writer avoids in great measure this difficulty and, as it is carried out directly in connection with the sugar determination, effects a considerable saving of time.

100 grams of the finely-grated pulp are washed upon a muslin filter with repeated quantities of cold water, until the filtrate

amounts to 2 liters; the muslin is squeezed after each addition of water, as already described under the determination of sugar. In this way practically all of the starch is washed out of the pulp. The filtrate, after being well mixed, is transferred to a tall beaker or cylinder, where it is covered and allowed to stand in a cool place over night. The finely suspended particles of starch will have completely settled by this time to the bottom of the vessel, forming a compact mass. The liquid above the starch is then removed by means of a siphon or decantation down to within a short distance of the precipitate; this solution may be used for the determination of sugars and malic acid.

The precipitate of starch is transferred with small quantities of cold water to a hardened filter-paper and washed to remove the last traces of sugar: 100 cc. of water are usually sufficient for this. The starch thus prepared consists of a white crumbly mass, but is not perfectly pure, owing to the presence of some cellular and albuminoid matter. The starch might be determined at this stage with sufficient accuracy by direct inversion with hydrochloric acid as in the Sachsse method, but the writer has preferred to use the more exact process of first hydrolyzing with diastase.

A starch determination by means of the diastase method should also be made upon the residue left on the muslin filter after the washing, in case the latter should show any reaction with iodine. The writer has never found the residues to yield more than 0.1 or 0.2 per cent. of starch upon the original pulp, so that the determination is rarely necessary if the washing has been properly performed.

The official diastase method¹ was followed throughout, except as regards the neutralization after the inversion with hydrochloric acid. The writer has always preferred a 10 per cent. solution of sodium hydroxide, using phenolphthalein, instead of sodium carbonate as prescribed in the official method; the troublesome frothing incident to the use of the latter substance is thus avoided.

Marc.—This represents that part of the fruit, which is insoluble in water. It is best found in connection with the sugar determination; the residue left upon the muslin filter after the

¹ Bulletin No. 46, revised edition, U. S. Department of Agriculture, Division of Chemistry.

washing, is transferred to a dish and dried to a constant weight at 100°C . With the exception of a trace of ash and albuminoid matter, the marc of apples was found to consist almost wholly of cellulose, lignin, and pentosans.

In case the percentages of the different marc constituents are desired, the pentosans are best determined by distilling a weighed amount of the dry marc with successive quantities of 12 per cent. hydrochloric acid, and precipitating the furfural in the distillate by means of phloroglucin.¹ The cellulose is separated from the other marc constituents by the chlorination process of Cross and Bevan.² The lignin³ bodies are estimated by the difference between the cellulose and pentosans and total marc, after correcting for the slight quantities of ash and albuminoid matter.

Malic and Acetic Acids.—No attempt was made by the writer to separate the various fruit acids in the analyses previously tabulated. The free acid was determined in every case by titration with decinormal soda, and calculated to malic acid. Besides the free organic acid, a considerable amount of the fruit acids exists in a combined form; the amount of this can be estimated from the alkalinity of the ash. In case of ciders and vinegars, where acetic acid is present, the latter is first removed by steam distillation, and determined by titration with decinormal soda solution; the distillation should be continued until 50 cc. of the distillate shows a neutral reaction. The solution left in the flask after the steam distillation is then titrated and calculated to malic acid as before.

Pectin.—This was determined by evaporating a definite amount of the fruit extract, juice, etc., to a small volume and precipitating with a large excess of 95 per cent. alcohol. After standing over night the precipitate was collected in a Gooch crucible, and washed with alcohol to remove all sugar. The precipitate was then dried at 100°C . to constant weight, and after incineration the weight of ash deducted and the loss estimated as pectin.

Other ingredients given in the preceding tables, such as fat, protein, etc., were determined according to the official methods of the agricultural chemists, and require no special description.

¹ For full description of the phloroglucin method for pentosans, see Bulletin No. 46, revised edition, U. S. Department of Agriculture, Division of Chemistry, p. 25.

² Cross and Bevan: "Cellulose," p. 95.

³ See article by Sherman: This Journal, 19, 305.

THE IDENTIFICATION AND PROPERTIES OF α - AND β -EUCAIN.¹

BY CHARLES LATEROP PARSONS.

Received September 24, 1901.

TWO new alkaloids under the names α -eucaine and β -eucaine have recently been offered to the medical and dental professions for use as a local anesthetic. There is scarcely a reference to either in any strictly chemical journal but their use and physiological properties have been very fully discussed in medical and pharmaceutical publications. Although they are proprietary drugs the fact that β -eucaine is so often substituted for cocaine, in dental preparations, hay fever remedies, and other proprietary medicine, makes it highly desirable that their distinctive properties be carefully studied and that methods be found for their identification and separation from cocaine and other alkaloids. It was owing to the fact that I was called upon to analyze a special dental preparation containing eucaine that my attention was first called to the existence of the alkaloid, and I was greatly handicapped by the silence of chemical literature upon the subject.

α -Eucaine was first obtained by George Merling² by synthesis from triacetonamine through triacetonamincyanhydrin to triacetalkamincarbonic acid, which, by the action of benzoyl chloride and subsequent action of methyl iodide in caustic potash solution, becomes *n*-methylbenzoyltetramethyl- γ -oxypiperidincarbonic acid methylester or " α -eucaine". This, when treated with hydrochloric acid, acts like other alkaloids forming a hydrochloride, in which form it is prepared and sold.

β -Eucaine was discovered by Albrecht Schmidt and George Merling³ and was obtained by purifying the vinylidiacetonamine of Fischer⁴ and substituting a benzoyl group for the hydrogen atom of the hydroxyl. Thus " β -eucaine" or benzoylvinylidacetonalkamine, is also an alkaloid which, when treated with hydrochloric acid, forms the hydrochloride.

It will be seen from the structural formulas of α - and β -eucaine

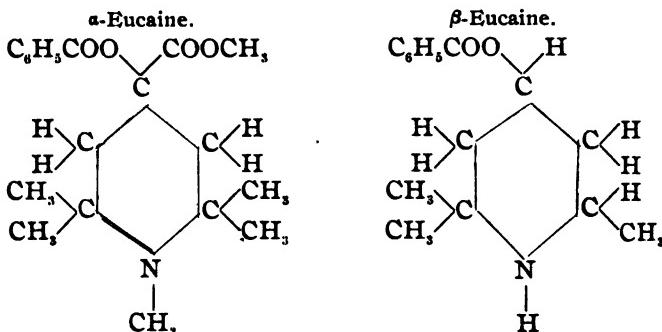
¹ Read at the Denver meeting of the American Chemical Society, August 29, 1901.

² *Apoth. Ztg.*, (1896), p. 293, 418, 448.

³ *Virchow's Archives für path. Anat. und Phys.*, (1896), vol. 148.

⁴ *Ber. d. chem. Ges.*, 17, 1894.

that they have a close relation to cocaine and to tropacocaine.



It was this close chemical connection which led to the belief that they would show similar anesthetic properties.

It is not the purpose of this paper to enter into a discussion of the physiological and therapeutic effects of the eucaines but it is not out of place to state that the chief claims of their superiority over cocaine are that they are far safer to use, that they cause no excitation of the heart's action, that β -eucaine, especially, is some four or five times less toxic, that they have equal analgesic power with cocaine, that they do not decompose by boiling and their hydrochlorides can hence be easily sterilized, and that their solutions will keep for an indefinite time without decomposition. The quite extended use of β -eucaine would seem to show that many of these claims have been substantiated. It would be well to add that α -eucaine has at times an irritating action or smarting effect of its own before anesthesia sets in, which has rendered its acceptance and use somewhat doubtful. It is claimed that this is absent with β -eucaine or at least is no more often the case than with cocaine. β -eucaine is the one that is almost exclusively used and the firm which manufactures both furnishes only β -eucaine when "eucaine" alone is called for. Accordingly almost all preparations on the market consisting in part of eucaine contain β -eucaine hydrochloride and the question of analysis would generally be a distinction between this salt and cocaine.

To establish means of identification of eucaine, all the well-known reactions of the alkaloids have been tried and I have endeavored to find new ones applicable to this particular case.

In general the properties of the eucaine alkaloids follow those of the strychnine group and especially do they very closely

resemble cocaine. The bases themselves are readily soluble in benzene, chloroform, ether, chloroform-ether, petroleum ether or gasoline, and amyl alcohol. They can be easily extracted from their salts by rendering their solutions in water slightly alkaline with ammonia and shaking out with any of the above solvents. This extraction is, however, most rapidly accomplished with light petroleum distillates or with ether. α -Eucaine melts at 103°, β -eucaine at 91°, and cocaine at 98°. In following out any scheme of analysis of the alkaloids they will probably always be found where cocaine would be expected and their identification becomes essentially a separation from each other and cocaine. α - and β -eucaine are sold in the form of their hydrochlorides and it is upon this salt that most of the tests for their identification should be made. As usually prepared, α - and β -eucaine hydrochlorides are white powders, identical in appearance. They are, however, easily crystallizable.

α -Eucaine hydrochloride melts at about 200° C. and decomposes at the same time. It is soluble at ordinary temperatures in about ten times its weight of water, solubility varying with temperature. It is more soluble in hot water, from which it crystallizes out to an approximately 10 per cent. solution on cooling. It is soluble in about its own weight of alcohol, 10 grams requiring from 8 to 9 grams of alcohol for solution. It is but slightly soluble in ether or olive oil, but glycerol dissolves it much the same as water.

β -Eucaine hydrochloride melts at 268° C. with decomposition. At ordinary temperatures it is soluble in water to the extent of about 3 per cent., but is more than twice as soluble in hot water from which most of the excess crystallizes slowly after cooling. Its solubility in alcohol is greater than in water or about 11 per cent., varying somewhat with the temperature. This comparative insolubility is one of its chief characteristics especially differing from cocaine hydrochloride which dissolves in less than its own weight of either water or alcohol. It is almost insoluble in ether or olive oil.

REACTIONS IN WHICH THE HYDROCHLORIDES OF α -EUCAINES, β -EUCAINES AND COCAINE ACT ALIKE.

Mayer's reagent gives with either α - or β -eucaine a light yellowish amorphous precipitate.

Wagner's reagent gives a voluminous reddish brown precipitate even in dilute solutions.

Tannic acid (1 : 10) gives no precipitate or only a very slight transparent flocculence.

Picric acid (1 : 100) yields a fine lemon-yellow precipitate, in solutions stronger than 1 per cent., which is soluble in acids, but in dilute solutions yields no precipitate. Even in moderately strong solutions the precipitate formed by the first drop or two of reagent redissolves. The precipitate with α -eucaine is more insoluble than either of the others, and comes down accordingly, in somewhat more dilute solutions.

Iodine in alcohol yields a brown precipitate soluble in excess.

Fröhde's reagent (sulphomolybdic acid) gives no precipitate.

Mercuric chloride (1 : 20) gives no precipitate in dilute solution but in moderately strong solutions gives a fine white precipitate, easily soluble in excess.

Ferric chloride and potassium ferricyanide mixed give no precipitate except a white one in strong solutions. Allen¹ states that cocaine gives a precipitate of Prussian blue, but I have not been able to obtain it. Ferric chloride is stated by some authors to turn red on boiling one or two drops of a dilute solution with cocaine, owing to the formation of benzoate of iron. But as it also turns red with either of the eucaines or simply with distilled water the reaction is of no value. It gives no precipitate even in strong solution.

Cadmium iodide gives a white precipitate.

Potassium ferrocyanide gives in solution of about 10 per cent. a slight colorless gelatinous precipitate. A saturated solution of β -eucaine does not yield this precipitate probably because the solution is too weak.

Potassium ferricyanide gives a white precipitate in moderately strong solutions, which is more easily thrown down if solution is acid with hydrochloric acid.

Potassium bromide, chloride, or bromate give no reaction.

If a few drops of a solution of either of the hydrochlorides of α - or β -eucaine or cocaine be acidified with strong nitric acid, evaporated to dryness in a watch-glass, and treated with 1 or 2 drops of a solution of alcoholic potash, a very characteristic odor of benzoic ethyl ester is obtained. This reaction would probably also be given with other alkaloids containing the benzoyl group.

¹ "Commercial Organic Analysis," Vol. III, part II, p. 275.

REACTIONS CHARACTERISTIC OF α -EUCAINE SALTS.

Potassium iodide (1 : 10) gives, in even moderately dilute solutions of α -eucaine hydrochloride, a white silky and glistening precipitate. This precipitate has much the same appearance as the one obtained when stannous chloride is added to a cold dilute solution of mercuric chloride. β -Eucaine and cocaine give no reaction.

Ammonia, even in dilute solution, precipitates the bases α - or β -eucaine or cocaine, but α -eucaine is almost insoluble in excess. In 1 per cent. solution the white precipitate is at once thrown down, and in the case of β -eucaine or cocaine dissolves immediately on addition of about their own volume of strong ammonia. α -Eucaine, so precipitated, can be diluted at least ten times with strong ammonia without solution. In stronger solutions the difference still exists but is not so easily recognized. A 3 per cent. solution of β -eucaine or cocaine requires about five times its own volume of ammonia to be dissolved and stronger solutions much in proportion to the per cent. present. In other words a strong solution of ammonia will dissolve about one-half of one per cent. of the bases β -eucaine or cocaine, while it will dissolve but a very small fraction of a per cent. of α -eucaine. In dilute solutions this is a very characteristic reaction for α -eucaine and strong solutions are, of course, very easily rendered dilute for the test.

Potassium dichromate, in strong solution, added drop by drop to a 0.5 to 1 per cent. solution of α -eucaine, begins to throw down a fine lemon-yellow precipitate after addition of 1 or 2 drops. The precipitate is then much increased by 1 or 2 drops of strong hydrochloric acid, and is then quite insoluble, dissolving only after several times diluting the volume of the solution. With stronger solutions the precipitation takes place at once, the first drop giving a more and more permanent precipitate as the solution grows stronger. The precipitate is notably insoluble in either water or hydrochloric acid. More dilute solutions either show no precipitate or only after addition of hydrochloric acid. Cocaine, 1 per cent. solution, is not precipitated by potassium dichromate, but the addition of 1 or 2 drops of concentrated hydrochloric acid throws down a yellow precipitate easily soluble in very slight excess of hydrochloric acid or on dilution of the solution with water. Weaker solutions do not precipitate while stronger solu-

tions precipitate at once. The precipitate is, however, easily soluble as before. β -Eucaine acts like cocaine. The precipitate in all cases is lemon-yellow. The α -eucaine precipitate is quite crystalline. All three may throw down a small amount of a yellow colloidal precipitate which sticks to the side of the test-tube and dissolves but slowly, although this in no wise interferes with the test and does not take place if reagents are added slowly. While this test depends upon the very much greater insolubility of the α -eucaine salt, the non-precipitation in dilute solutions of a certain strength until after the addition of hydrochloric acid is quite characteristic for all. The correct strength is about 0.5 per cent. solution of α -eucaine and about 1 per cent. for β -eucaine and cocaine. In the case of cocaine and β -eucaine, the test may be conveniently applied by precipitating a stronger solution than 1 per cent. with potassium dichromate solution, diluting carefully with water until precipitate just dissolves. On addition of a drop of concentrated hydrochloric acid the precipitate will at once re-form. This can not be done with α -eucaine for precipitate once formed it is difficult to get it to dissolve at all.

Chromic acid (1 : 20) acts similarly to the dichromate.

**REACTIONS OF COCAINE DISTINGUISHING IT FROM EITHER
 α - OR β -EUCAINE OR FROM BOTH.**

If a small amount of cocaine hydrochloride be rubbed up with dry mercurous chloride (calomel), and then moistened with alcohol, it rapidly turns to a grayish black. α -Eucaine hydrochloride becomes slowly a dark gray. β -Eucaine hydrochloride is not affected.

Platinic chloride throws down slowly a yellow crystalline precipitate from a 1 per cent. solution of cocaine hydrochloride which is insoluble in hydrochloric acid. α - and β -eucaine hydrochloride in 1 per cent. solution are not altered. In stronger solutions all three hydrochlorides are immediately precipitated by platinic chloride but the cocaine precipitate is not soluble in hydrochloric acid while the precipitates by either eucaine are at once dissolved.

F. Giezel¹ has pointed out that the permanganate of cocaine is much more stable than that formed by most other alkaloids. This fact gives rise to one of its most distinguishing reactions.

¹ *Pharm. Ztg.*, p. 132 (1896).

The test is best applied upon a microscopic slide or in a small watch-glass. A drop of a solution of the hydrochloride is placed upon the glass and a very small drop of a solution of potassium permanganate is added. If the solution is strong enough for a precipitate to appear at once the change can be observed on the precipitate but it is preferable to watch the change of color of the solution itself. With either of the eucaines the color almost immediately begins to change to brown while with pure cocaine the original color holds generally for fully half an hour but also eventually changes to brown. The cocaine precipitate examined under the microscope is a beautiful violet-red which also in time turns to brown. This is true of the eucaine precipitates at first but they rapidly change to brown. Excess of permanganate should be avoided.

Cocaine hydrochloride in solution in either water or alcohol polarizes light strongly to the left. Antrich¹ states that this is the best test for the purity of the salt. According to this authority for aqueous solution $S_d = -52.2$ and for solution in alcohol of 0.9355 sp. gr., $S_d = -68.06$. A solution of the hydrochlorides of either α - or β -eucaine does not polarize light.

Cocaine when used in the eye almost always causes mydriasis. β -Eucaine does not dilate the pupil.

REACTIONS CHARACTERISTIC OF β -EUCAINE HYDROCHLORIDE.

The chief characteristic property of β -eucaine hydrochloride is its comparative insolubility in water and alcohol and it is readily distinguished from cocaine by this property. A small test sample of cocaine hydrochloride, if moistened with its own volume of alcohol or water, dissolves at once, while β -eucaine hydrochloride is little affected. In making the test, however, where weighed quantities are not used it should be remembered that even β -eucaine is soluble to the extent of 11 per cent. in alcohol and a too large amount of the solvent should not be used. Just enough to moisten is all that is necessary to dissolve cocaine or α -eucaine hydrochloride.

No chemical reactions of a positive character have been found characteristic of β -eucaine, but the results with permanganate, mercurous chloride, platinic chloride, and polarized light, will identify cocaine, while the tests with potassium iodide, potassium

¹ Ber. d. chem. Ges., 20, 310.

chromate and ammonia will distinguish it from α -eucaine. These with the other reactions noted will serve to separate it from other alkaloids.

MICROSCOPIC CHARACTERISTICS.

A careful examination of many of the precipitates which the various reagents yield with either of the eucaines or with cocaine failed to disclose any special characteristic of value. Many of them are beautifully crystalline and give striking displays of color with polarized light, but they vary too much with different conditions to be used with certainty as a means of identification. An examination of the alkaloids themselves as precipitated by ammonia and crystallized from chloroform also give negative results. Fortunately, however, the hydrochlorides, when pure, are easily identified under the polarizing microscope and especially is cocaine hydrochloride recognizable at once.

The slides are best prepared by allowing a drop of an aqueous solution to spontaneously evaporate. Cocaine under these conditions does not always crystallize at once even when quite dry. But if set aside for a few hours the crystals will form and the peculiar feathery and fan-shaped radiations, resembling very closely those seen on a broken nodule of wavellite, are recognizable even with the naked eye. The examination is most satisfactorily performed with a magnifying power of about 250 diameters.

α -Eucaine hydrochloride in saturated solution tends to crystallize in little spots which, under polarized light, look like very highly colored rosettes made up of very small crystals, so that the field is always bright, never showing any constancy of extinction directions. On edges of drop, the rosettes sometimes show small feathery forms of crystals of which the extinction directions vary but are more often diagonal. A 5 per cent. solution gives much the same result. The rosettes frequently appear to be made up of concentric rings of very small crystals, the center of rosettes being thicker than edges and only the edges showing plate or feather forms large enough to be examined as individuals. Interference colors are very bright. When crystallized from dilute solution the rosette forms may become very small and numerous, covering the entire field while the interference colors are only gray or black. The forms of gray and black overlying feathers

are at times very prominent in α -euclidean and resemble nothing so closely as the small feathers of Plymouth Rock poultry.

β -Euclidean hydrochloride from saturated solution shows broad feathery or fern-like forms, sometimes blade-like or tabular. Usually the tabular forms show concentric rings of high color around the edges and the extinction directions are easily determined. They are usually slightly oblique to the main axis of the crystal, but different crystals show two separate angles of extinction, one being the complement of the other and due to the fact that the individuals are viewed from opposite sides. The forms already mentioned are more apt to be found around the outer edge of the evaporated drop while the center is made up of isolated individuals which show brilliant tabular and prismatic forms sometimes quite small and rod-like. Rarely they are diamond-shaped. These diamond-shaped forms sometimes show extinction directions symmetrical to the main axis, but more often slightly oblique. The individual crystals are large and much more easily studied than those of α -euclidean. If more dilute solutions of less than 1.5 per cent. are used, the characteristics do not come out so plainly, the crystal forms being smaller and showing very low interference colors, mainly light grays. Also these sometimes show feathery forms and rosette forms something like α -euclidean.

Cocaine hydrochloride in 10 per cent. to 1 per cent. solution crystallizes in fan-like shapes. A 2 per cent. solution gives a solid field of radiating forms, the individuals of which resemble very closely the forms sometimes seen on a frosted window. Extinction is parallel and perpendicular to the main axis of the crystals. Colors are brilliant and the whole field is characteristic, enabling one to distinguish cocaine immediately. With dilute solutions the fan-like shapes are still marked, but the field is sometimes broken and interference colors are a low order of light grays.

In conclusion it is perhaps well to suggest that in working on unknown substances all tests for euclidean and cocaine, as with other alkaloids, are much more valuable when compared with those of samples whose identity is known.

SOME HYDROCHLORATED SULPHATES.

BY CHARLES BASKERVILLE.

Received August 16, 1901.

S MITH and Tunnell¹ have published experiments on the removal of the acid radical in sodium and potassium sulphates by gaseous hydrochloric acid under the influence of heat. The volatilization, rather substitution, of sulphuric acid by hydrochloric acid has been pointed out in papers presented before the North Carolina Section by the writer. Heusgen² had previously noted that gaseous hydrochloric acid acted upon potassium sulphate cold. Prescott³ observed substitution when the same salt and concentrated hydrochloric acid were evaporated together. Smith obtained addition products, *i. e.*, $K_2SO_4 \cdot xHCl$ (x not stated), in the course of the reaction, but a complete elimination of the sulphuric acid was not observed. The reaction is attributed to mass action.

Our observations on somewhat similar reactions were made with salts of zinc, cadmium, and mercury. The experiments demonstrate without doubt the effect of mass action, but time, temperature, and the removal from the sphere of action of certain agents involved have a decided influence on the observed changes.

The degree of substitution depends entirely upon the temperature and time of the action as well as mass. The preparation of new bodies like these is of no great importance. The point of interest rests in the graduated substitution of water by hydrochloric acid, molecule for molecule, in crystalline bodies. This substitution may throw some light upon the discussed "molecular compounds."

MERCURIC COMPOUNDS.

(WITH LIONEL WEIL.)

According to Berzelius, if a stream of hydrochloric acid gas be passed over mercuric sulphate, mercuric chloride and sulphuric acid will result. Ditte⁴ states that if gentle heat be applied, the mercuric sulphate combines with hydrochloric acid, melts and snow-white crystals of $HgSO_4 \cdot HCl$ are sublimed. Further the same compound may be obtained by evaporating mercuric sulphate and concentrated hydrochloric acid, or mercuric chloride and

¹ This Journal, 21, 930 (1899).

² Ber. d. chem. Ges., p. 1671 (1876).

³ Chem. News, 36, 178.

⁴ Ber. d. chem. Ges., 12, 361 (1879).

sulphuric acid with 1 molecule of water. By gentle heat, white needle crystals are obtained.

The experiments were repeated successfully in the following way: Twenty grams mercuric sulphate were treated with 20 cc. concentrated hydrochloric acid in a porcelain dish, the excess of acid being first driven off by a free flame; the substance was dried on a sand-bath and sublimed at 240° C. into a funnel, through which a rapid stream of air was drawn. The crystalline sublimate was treated in turn with alcohol and a mixture of alcohol and ether to remove the free acid and mercuric chloride and sulphate. The insoluble portion was not affected by hydrochloric acid and was only slightly soluble in nitric acid. It was fused with sodium carbonate, leached, and the chlorine determined.

	Calculated for $HgSO_4 \cdot HCl$	Found.
Chlorine.....	10.67	10.81

The yield was small and not improved by varying the amounts of the substances used.

In following out another method for preparing hydrochlorated mercuric sulphate, namely, by gently heating the mercuric sulphate in a stream of dry hydrochloric acid, only a small amount of the substance was obtained. A new white, crystalline, very deliquescent body was obtained however which proved on analysis to be the dihydrochlorated body, which is very soluble in water.

	Calculated for $HgSO_4 \cdot 2HCl$	Found.
Sulphur trioxide.....	18.65	18.18

Roscoe and Schlorlemmer state that mercuric chloride dissolves without decomposition in concentrated sulphuric acid. This seems to be true, but, on heating, a crystalline sublimate was obtained in the funnel suspended above the dish in which the reaction occurred. If the heating be too prolonged some free sulphuric acid will volatilize and condense on the crystals. Molecular amounts of mercuric chloride and $H_2SO_4 \cdot H_2O$ were carefully heated in a porcelain dish. Clean, dry, well-formed monoclinic crystals were selected from the sublimate in the neck of the funnel suspended above. On analysis these crystals gave the following results :

	Calculated for $HgSO_4 \cdot 2HCl \cdot H_2O$	Found.
Chlorine.....	18.34	19.89

The substance was not further worked with.

CADMIUM COMPOUNDS.

(WITH ISAAC F. HARRIS.)

By varying the temperatures we have succeeded in replacing variable amounts of water of crystallization in $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$. At 150° C . the sulphate loses 4 molecules of water; if subjected to the action of dry hydrochloric acid at that temperature 4 molecules of hydrochloric acid combine with the partially dehydrated body, giving $3\text{CdSO}_4 \cdot 4\text{H}_2\text{O} \cdot 4\text{HCl}$.

At 200° C . the hydrated sulphate permits all its water to be expelled, giving $3\text{CdSO}_4 \cdot 8\text{HCl}$. At that temperature under the prolonged influence of the hydrochloric acid, or at dull red heat for a shorter period, the sulphuric acid radical is displaced and finally CdCl_2 results. The observations noted took place with the hydrated sulphate, or material dried at 150° C . or completely dehydrated.

The bodies obtained are very deliquescent and present difficulties in obtaining them pure for analysis. Hydrochloric acid is held mechanically by the compounds and is difficult to remove. The method of procedure was to place the sulphates, hydrated and anhydrous, in a porcelain boat in combustion tubing fixed in an air-bath punctured to admit the tube. Dry hydrochloric acid was passed through the tube whose temperature was closely guarded. The material melted and crystallized out on cooling. If the temperature reached dull redness (with experiments over direct flame) the body was sublimed to the cooler portions of the tube. In order to remove the mechanically bound hydrochloric acid, the tube was allowed to cool for twelve hours, a steady stream of gas passing through all the while; afterwards dry air, free from carbon dioxide, was passed through for two or more hours. Some analyses are appended.

	Calculated.	Found.	
	I.	II.	
Original sulphate $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$	$\left\{ \begin{array}{l} \text{SO}_4 \\ \text{H}_2\text{O} \end{array} \right.$	$\left\{ \begin{array}{l} 31.2 \\ 18.7 \end{array} \right.$	$\left\{ \begin{array}{l} 31.4 \\ 18.1 \end{array} \right.$
$3\text{CdSO}_4 \cdot 4\text{H}_2\text{O} \cdot 4\text{HCl}$ (at 150° C)	$\left\{ \begin{array}{l} \text{HCl} \\ \text{SO}_4 \end{array} \right.$	$\left\{ \begin{array}{l} 17.00 \\ 28.00 \end{array} \right.$	$\left\{ \begin{array}{l} 16.00 \\ 28.00 \end{array} \right.$
With prolonged heating.....	$\left\{ \begin{array}{l} \text{HCl} \\ \text{SO}_4 \end{array} \right.$	$\left\{ \begin{array}{l} 22.5 \\ 23.5 \end{array} \right.$	
Fused and partially volatilized $3\text{CdSO}_4 \cdot 8\text{HCl}$	HCl	31.00	30.1
Continued heat and sublimation CdCl_2	Cl	38.6	38.00

A few experiments were made with zinc sulphate and the above observations extended, but not completed.

UNIVERSITY OF NORTH CAROLINA,
April 23, 1901.

THE ACTION OF ZINC ETHYL UPON NITRO AND NITROSO COMPOUNDS.

(A REPLY TO I. BEWAD.)

BY ARTHUR LACHMAN.

Received September 28, 1901.

In a recent paper containing a wealth of experimental material, I. Bewad undertakes to prove the complete analogy of the action of zinc ethyl on carbonyl compounds on the one hand, and upon nitrogen-oxygen compounds on the other. This work was begun about fourteen years ago,¹ but its most important results were not manifest, or at any rate were not published in accessible journals, until last year.² In his last paper Bewad is anxious to claim priority for these results, evidently with reference to my own publications,³ since the general subject has not been investigated by any third party.

Bewad's priority in this work is unquestioned. In fact, it was through a study of Bewad's own publications that I was led to attempt the main problem I have undertaken; *viz.*, the intimate structure of the nitro group. Priority, however, is no guarantee of accuracy; and since Bewad has been, and is still, in error as to some matters of fact, and is entirely at sea with his explanations of other facts, I have thought it desirable to clear up several points that would seem reasonably certain, before proceeding with new experimental work.

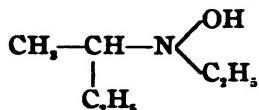
In order to indicate that Bewad's results in the past have needed revision, let me briefly append a history of events. In his first papers (*cf.* above), Bewad asserted the following: That the action of zinc ethyl on nitroethane gave triethylamine oxide, $(C_2H_5)_3N = O$; that the reaction succeeds with only one molecule of zinc ethyl; that if two are taken, no amine oxide at all is obtained; that upon reduction the amine oxide forms triethylamine. On the other hand, I showed in my first paper that if two molecules of zinc ethyl are taken the yield of "amine oxide,"

¹ *Cf. Ber. d. chem. Ges.*, **21**, ref. 479 (1887); **22**, ref. 250 (1888).

² *J. prakt. Chem.*, **63**, 94 (1901).

³ *Am. Chem. J.*, **21**, 433 (1899); *Ber. d. chem. Ges.*, **33**, 1022 (1900).

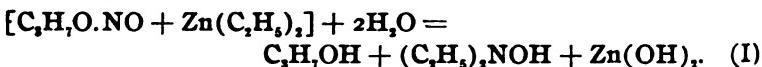
instead of vanishing, is more than doubled (a discovery which Bewad seems to have made for himself subsequently). But what is most important is that no amine oxide whatever is formed, but instead ethyl-sec. butylhydroxylamine,



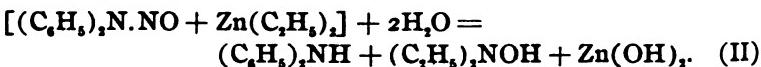
Bewad was fortunate enough to discover this for himself. The previously noted reduction to triethylamine was erroneous.

My own work on the nitro group took its start from the then unquestioned existence and method of formation of triethylamine oxide. All of the conclusions contained in my first publication are therefore futile, and are herewith withdrawn.¹ To be sure, the real triethylamine oxide has subsequently been found by Dunstan and Goulding,² and by myself,³ but its method of formation does not bring it into connection with the nitro group.

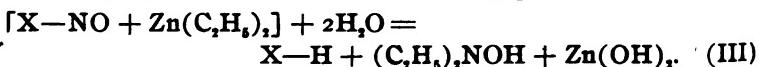
It is to Bewad's explanation of the mechanism of his results, however, that I wish to call attention. To begin with the facts first, Bewad has found that when aliphil nitrites are treated with zinc ethyl and then with water, the products are alcohols and diethyl hydroxylamine (and of course zinc hydroxide); *e.g.*,



On the other hand, I have found that when diphenylnitrosamine is treated with zinc ethyl, the products are diphenylamine and diethylhydroxylamine :



If we designate, in these two equations, the group attached to —NO by X, the two reactions are exactly parallel :



It is a reasonable assumption that the mechanism of this reaction is identical in both cases.

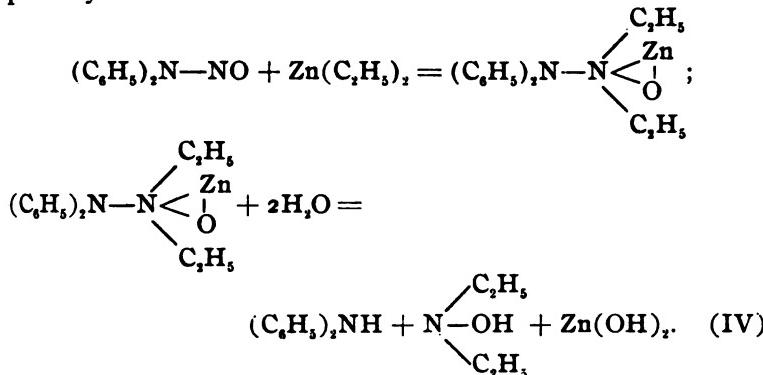
In (II), I was able to show, by separating and analyzing the first product, that one molecule each of nitrosamine and zinc ethyl

¹ *Am. Chem. J.*, 21, 440 (1899).

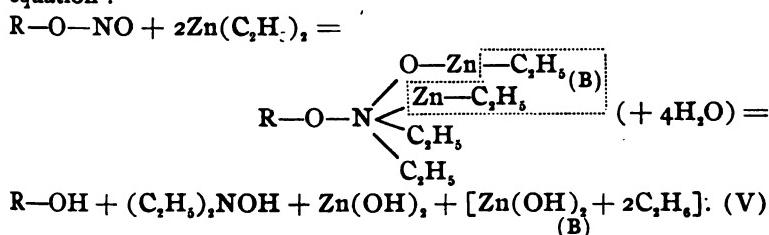
² *J. Chem. Soc.*, 75, 792 (1899).

³ *Ber. d. chem. Ges.*, 33, 1025 (1900).

unite to form a stable compound, which is subsequently decomposed by water :



The decomposition products agreed closely with the calculated yield (diphenylamine quantitative, hydroxylamine over 50 per cent.). Bewad, on the other hand, led by the analogy of the carbonyl group, —CO, assumed that two molecules of zinc ethyl would be required, did not try to use merely one, did not separate or analyze his addition product, and gives the following equation :



I have labeled the two zinc ethyl molecules in order to point out that molecule (B) simply adds on to the first product, and then splits off again, for no other apparent purpose than to gratify Bewad's sense of analogy.

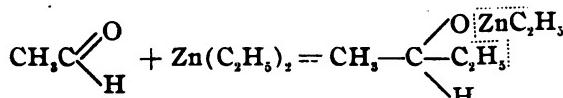
From the above it would appear that we have a very general reaction of the nitroso group when not attached directly to carbon. In this latter case, I have found nitrosobenzene to behave altogether differently, for reasons that cannot yet be understood.¹

One seeks in vain for any analogy between this general reaction of nitroso compounds and the behavior of carbonyl groups with zinc ethyl. Bewad compares the former to the reaction of alde-

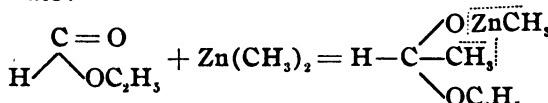
¹ Cf. Am. Chem. J., 21, 442 (1899).

hydes, formic and oxalic esters, etc.¹ But in all of these instances one molecule of zinc alphyl is able to introduce only one hydrocarbon radical.

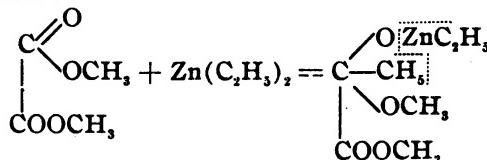
Aldehyde :



Ethyl formate :

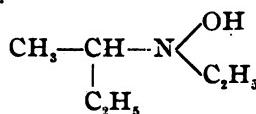


Methyl oxalate :



The behavior of the nitroso group is therefore unique, and in no way parallel to that of carbonyl.

The behavior of nitro compounds with zinc ethyl is much more complicated. As Bewad's equations are highly complex, as he is guided wholly by the misleading carbonyl analogy, and as some of his formulas are self-contradictory, it is not necessary to devote further time to this side of his work. The facts are more important for the present. Bewad finds that zinc ethyl and nitroethane react slowly. If the mixture is decomposed after a few days, the main products are unchanged nitroethane and secondary nitrobutane. If allowed to stand several months, the nitro-paraffins diminish in amount, and the main product is then ethyl sec. butyl hydroxylamine :

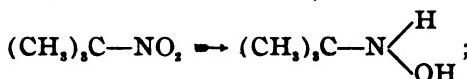


An entirely similar reaction was obtained with numerous other nitroparaffins and zinc alphyls, provided that primary or secondary nitroparaffins are taken. (Zinc methyl with nitromethane forms an exception.)

¹ Loc. cit., p. 110.

It is not worth while to supplement Bewad's speculations by others equally unfounded ; but the following facts seem to stand out plainly. First, that the primary action of zinc alphyl is to alkylate, and that this alkylation is independent of the subsequent alteration of the nitro group ; proof : nitrobutane is formed before the hydroxylamine. Second, that the new nitroparaffine thus formed is not present in the free state, but probably in the shape of a zinc alphyl salt ; proof : if a primary nitro compound is the original substance, the resulting hydroxylamine contains a secondary radical ; whereas if we start from a secondary nitroparaffin, we get a tertiary radical in the hydroxylamine. If free secondary nitroparaffins are first formed, we should obtain tertiary radicals in both instances. Third, that this intermediate product is capable of adding on zinc alphyl in such a way that one hydrocarbon radical attaches itself to nitrogen. This addition depends upon the previous compound, and is not wholly due to the nitro group.

The last conclusion needs further details. Bewad, in an experiment to which he himself attached but little importance, found that a tertiary nitroparaffine was simply reduced to the corresponding hydroxylamine without alkylation,



the absence of a mobile hydrogen atom, with its consequent replacement by zinc alphyl, seems to prevent alkylation of the nitrogen atom.

On the other hand, we may have here a specific reaction of the nitro and the nitroso group when directly attached to carbon. The main product when nitrosobenzene acts upon zinc ethyl is phenylhydroxylamine.¹ Nitrobenzene also gives a small amount of phenylhydroxylamine.² Bewad found only aniline in this last case, but that is an error in fact ; besides phenylhydroxylamine, I was able to isolate small amounts of aniline and ethyl aniline. Here again it will be best to refrain from speculative equations until further facts are obtained.

It is clear, however, that in the action of zinc ethyl on nitrogen oxygen compounds we have a process that is by no means analogous to the behavior of carbonyl compounds ; that different

¹ Lachman : *Am. Chem. J.*, 21, 343 (1899).

² *Ibid.*

classes of these nitrogen oxygen compounds behave altogether differently ; and that only for the very limited group of nitroso compounds whose nitrogen atom is not directly linked to carbon is there anything like a clear comprehension of the details of the reaction.

EUGENE, OREGON,
August, 1901.

REVIEW.

A REVIEW OF SOME RECENT PROGRESS IN ORGANIC CHEMISTRY.¹

It is with deep regret that I am obliged, at this first attempt of the Section, to bring a systematic review of recent progress in chemistry, to ask your kind indulgence for the many omissions and defects in this summary of the recent history of organic chemistry. The time at my disposal has been very short ; the subject-matter, I need not say, is all too extensive. A pains-taking German statistician has calculated that over 10,000 pages are needed to record the annual progress of organic chemistry. I have endeavored to report upon the work of some three years ; the printed pages, if laid side by side, would make a solid field of type covering some 6,000 square feet—a large area for a critic to weed over by lamplight. Under the circumstances, I have ventured to select a few of what have seemed to me the more important achievements, and have called this paper "A Review of Some Recent Progress."

NOMENCLATURE AND REGISTRATION.

The important problem of naming organic compounds has not advanced much beyond the work of the Geneva conference in 1893. It will be remembered that the Geneva rules are fairly satisfactory only for the simpler fatty compounds ; they are too cumbersome for complex fatty derivatives, and fail almost completely with the vast majority of ring compounds. It is still possible for ten chemists to describe one and the same substance under ten different names, without recognizing the identity of their descriptions. An important discovery by M. M. Richter, however, promises to be of great assistance in simplifying this difficulty. Richter has pointed out that while the name of an organic compound may not be characteristic, its *empirical composition is absolutely definite*. He has, therefore, undertaken the truly Herculean task of gathering nearly 80,000 organic substances together into a dictionary, grouping these according to the increasing complexity of their atomic composition. The result is a

¹ Read at the Denver meeting of the Society, August, 1901.

monumental work,¹ whose use enables the chemist to identify an unknown compound in the shortest possible time.

At first sight, it may appear that the Richter system has serious disadvantages. For instance, no less than 52 compounds of the formula $C_{12}H_{16}O_3$ are to be found in this dictionary. Even if we should ascertain this formula for a newly-found substance, a huge problem remains. On the other hand, it is to be observed first, that Richter is not responsible for the isomerism of these 52 compounds; and second, that by thus grouping them all together in one place, the comparison of data is greatly facilitated. As a matter of fact, the most superficial determination of properties, once the composition is known, is all that is needed to pick out the desired name from the list. The ability of the Richter system to stand the test of actual use is shown by its adoption for the index of several important journals; *e. g.*, the *Berichte*, the *Annalen*, and the *American Chemical Journal*.

This general use of Richter's system is interesting from two rather different points of view. For one, it will serve to increase the respect of the organic chemist for quantitative analytical work. He has been compelled to identify his substances largely by their general reactions and relationships. He has even been proud of his skill in dispensing with analysis. But the analytical route is now the shortest method of identifying substances, and the organic chemist must again be broiled over his combustion furnace as in Liebig's time. I venture to predict a speedy improvement of this venerable contrivance.

The second feature takes a speculative turn. The present development of organic chemistry is due to the discovery of isomerism; *i. e.*, of the fact that *empirical composition does not suffice to characterize a substance*. It is curious that the fruits of this discovery should bring us back to one of the earliest ideals of modern chemistry. How this would have pleased Berzelius!

In the way of special propositions in nomenclature, it is worth while to note the suggestions of Vorländer,² that *all* univalent hydrocarbon radicals, both fatty and aromatic, be designated by the old term *alkyl*; that fatty alkyls be called *alphyls*, and aromatic alkyls be named *aryls*. Mixed fatty and aromatic radicals, such as benzyl, are to be called *alpharyl*. Acid radicals are to have the class name *aryl*, from which are then derived *alphacyl* and *aracyl* for fatty and for aromatic acid radicals, respectively. These suggestions seem to have been widely adopted.

The need of some comprehensive method of naming and registering organic compounds has been shown by Rey and by Kaufman, in rather alarming fashion. Assuming not more than nine different substituents, hydrogen included, in the naphthalene

¹ "Lexikon der Kohlenstoffverbindungen."

² *J. prakt. Chem.*, **59**, 247 (1899).

³ *Ber. d. chem. Ges.*, **33**, 1910, 2131 (1900).

nucleus, 10,766,601 derivatives are possible. Organic chemistry is not likely to perish for lack of material, it would appear.

We cannot do more than refer here to Baeyer's proposed nomenclature for the so-called condensed carbon rings.¹ As with all of Baeyer's proposals, this one is sure to be universally employed.

MISCELLANEOUS COMPOUNDS AND REACTIONS.

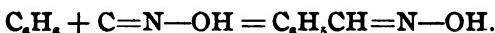
Under this heading will be given a number of interesting or important facts that cannot well be classified under other topics. The order of arrangement is merely one of convenience.

The *paraffin hydrocarbons* will soon no longer deserve their name. The difference between them and the aromatic hydrocarbons, once so marked, has been shown by Worstell to be only a matter of degree.² They are attacked both by concentrated nitric and sulphuric acids, yielding nitroparaffins and sulphonlic acids, just as benzene does. The action is much slower than in the latter case, however, and seems to reach its equilibrium at a much lower percentage of transformation.

In the *sugar group*, Ruff³ has discovered a new method of passing from one sugar to the next lower in the series. This method consists in the oxidation of the calcium salts of the corresponding acids with hydrogen peroxide. He was thus able to prepare *d*-erythrose from *d*-arabinose, and to establish the generic relationship of the former to the sugar series.

Graphitic acid, obtained by the oxidation of graphite, has long been regarded as one of the mysteries of chemistry. It has recently been investigated by Staudenmaier,⁴ who concludes that it is likely to remain a mystery for some time to come. The formulas and properties that have been previously ascribed to its various derivatives are entirely unreliable. Staudenmaier has found a very easy method of preparing the acid, suitable for lecture demonstration.

It will be remembered that a few years ago Nef was able to bring to a conclusion a century's work on *fulminic acid*, by showing that this interesting acid is the oxime of carbon monoxide, C=N—OH. This has recently been substantiated in a curious manner by Scholl.⁵ The Friedel-Crafts reaction of mercury fulminate, benzene and aluminum chloride leads to the synthesis of benzaldoxime:



The Friedel-Crafts reaction itself, which Baeyer has called the magic trunk of the wizard because of the wonderful things it

¹ *Ber. d. chem. Ges.*, **33**, 3771 (1900).

² *Am. Chem. J.*, **21**, 210 (1899); **20**, 664 (1898).

³ *Ber. d. chem. Ges.*, **32**, 3672 (1899).

⁴ *Ibid.*, **32**, 2824 (1899).

⁵ *Ibid.*, **32**, 3494 (1899).

furnishes in inexhaustible supply, has been the object of careful study by Perrier¹ and others; and before long we may hope to understand this important process to a degree befitting its importance.

The bitter struggle over the constitution of the *diazo compounds* is drawing to a close. It will be remembered that Hantzsch has contended for a stereochemical explanation of diazo isomerism, whereas Bamberger stood out for a structural explanation of these phenomena. It would take us too far afield to enter into the details of this controversy here, and a few observations must suffice. Bamberger for the last three years has been allowing his case to go by default, a sign that he has recognized his defeat. Quite recently he has made an important admission of error with reference to the metallic derivatives of the diazo compounds. Hantzsch, meanwhile, with the agility that has characterized the evolution of his views, has returned to the proposition he had so strenuously opposed at first, that the isodiazos are true nitrosamines in the free state. In connection with the diazo compounds, Hantzsch has elaborated a new theory of chemical processes which will be considered below.

The *uric acid* group is witnessing a decided "boom" during the last few years. Fischer's syntheses in this group are too well known to refer to now. W. Traube has recently discovered an entirely new synthesis of uric acid and its numerous congeners.² The method is too complex for description here; suffice it to say that it starts with cyanacetic acid, a compound easy to obtain in large quantities, and that Traube has already succeeded in obtaining xanthine, guanine, uric acid, and numerous alkylated derivatives of these. The yields are said to be almost quantitative.

The remarkable activity of investigation and synthesis in the uric acid group undoubtedly owes its origin to the hope of commercial success. Fischer's work has shown a very close connection between caffeine and uric acid; and a moderate fortune awaits him who will be able to prepare caffeine cheaply by a synthetic process. Aside from this material interest, however, the uric acid group occupies an important position in the purely scientific aspects of chemistry. On the one hand, the function of uric acid and its derivatives within the animal organism is a topic of the profoundest importance to physiology and dietetics. Great progress is to be expected when the advertisements of the Michigan "health food" people will be published in befitting detail in the *Berichte*. And on the other hand, a very curious isomerism has been brought to light among the mono-methyl uric acids. Four of these are foreseen by structural theories, whereas Fischer and Ach³ have already discovered six. No explanation is offered

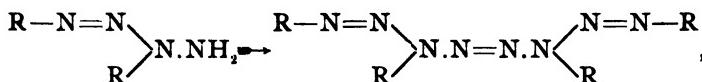
¹ *Ber. d. chem. Ges.*, 33, 815 (1900).

² *Ibid.*, 33, 3035 (1900).

³ *Ibid.*, 32, 2723 (1899).

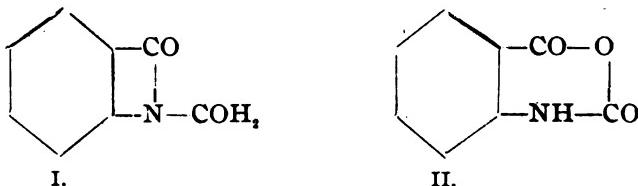
so far, except that Fischer, than whom no man is a better judge, has expressed his conviction that stereochemistry and tautomerism have no application here.

Among the large number of curious *nitrogen compounds and reactions* discovered during the past few years, a few must answer for the present. A long chain of nitrogen atoms has been prepared by Wohl and Schiff.¹ By oxidation of the so-called diazo-hydrazides,



which contain four nitrogens in a chain, octazons with eight atoms are produced. The mere existence of these chains is an important contribution to our knowledge of the combining power of nitrogen.

Another interesting datum with reference to this combining power is found in the structure of isatoic acid. Erdmann² has shown that this acid, which for a long time was supposed to have the formula I, really has the formula II:

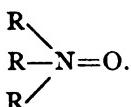


The interesting feature of this discovery, which Erdmann seems to have missed, lies in the fact that until now isatoic acid was the only substance which had a free carboxyl group, —COOH, directly attached to nitrogen. Carbamic acid, H₂N—COOH, for example, is incapable of existing in the free state, and is known only in the shape of salts, esters, and other derivatives. It has now been shown that isatoic acid possesses a different structure than the one formerly assigned to it, so that we are forced to regard the combination of a carboxyl group with nitrogen as one of the incompatibilities of nature.

A third interesting discovery in the nitrogen territory was made independently by Wolffenstein, Bamberger, and Dunstan and Goulding. These investigators found that basic nitrogen atoms, as contained in the various amines, can be directly oxidized with hydrogen peroxide, yielding hydroxylamine derivatives. The most curious of these are the amine oxides, of the general formula

¹ Ber. d. chem. Ges., 33, 2741 (1900).

² Ibid., 32, 2159 (1899).



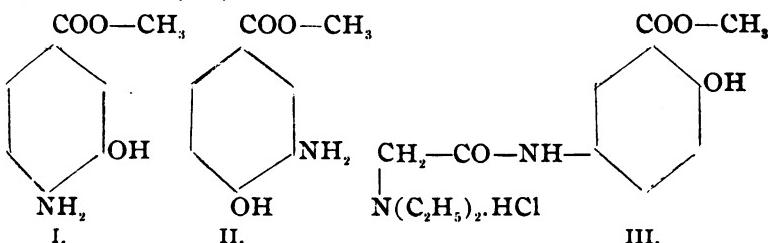
The amine oxides will play an important part in the future history of nitrogen.¹

More or less connected with the chemistry of nitrogen, though in a manner by no means understood, are the *artificial medicaments*. It is a remarkable fact that very many of the most powerful drugs, including, of course, all the alkaloids, contain nitrogen. This is true of the artificial as well as of the natural members of the *materia medica*. I need only instance phenacetine and antipyrine. The study of the connection between chemical compositions and physiological action is steadily progressing, and the time seems not far distant when the scientific practitioner will invent new compounds off-hand at the bedside, instead of relying upon the *pharmacopoeia*. A long step in this direction has been taken by Einhorn,² who by systematic planning has obtained three new substitutes for cocaine :

Orthoform, *p*-amido-*m*-oxybenzoic methyl ester (I).

Orthoform new, *m*-amido-*p*-oxybenzoic methyl ester (II).

Nirvanin diethylglycol-5-amido-2-oxybenzoic methyl ester hydrochlorate (III).



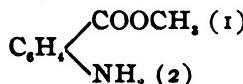
These anesthetics found immediate entrance into medical practice.

Attention should be called to a curious fact in all of the above formulae : viz., that the *methyl* esters of the various substituted benzoic acids have been selected. The corresponding *ethyl* esters have no marked anesthetic properties. Here is a flagrant breach of the law of homology, which calls for protest from the systematists. It is a common statement in text-books of organic chemistry that all the members of a homologous series have identical chemical properties ; yet here we find the simple substitution of ethyl for methyl annihilating the most characteristic property of some rather complicated compounds. This remarkable influence

¹ Cf. Lachman : *Ber. d. chem. Ges.*, **33**, 1038 (1900).

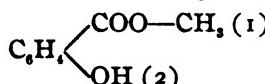
² *Ann. Chem. (Liebig)*, **311**, 33 ff (1900).

of the methyl group is not confined to drugs. It has recently been found that the *methyl ester of anthranilic acid*,



is one of the essential odorous principles of the orange blossom and the jasmine.¹ The corresponding *ethyl anthranilate* is almost odorless.

A similar instance is to be found in the esters of salicylic acid; methyl salicylate is the oil of wintergreen,



whereas ethyl salicylate has only a faint ethereal odor.

The above investigation of orange and jasmine oils furnished an additional surprise; for it transpired that the sweet, penetrating perfume of these flowers was due in no small part to *indol*!! Indol, a constant ingredient of feces, has long been noted for its penetrating qualities; its sweet perfume comes as a surprise to many a patient, long-suffering chemist. Yet there seems to be no doubt that pure indol has a decided perfume odor, and that the disagreeable smell of the substance as usually obtained is due to some impurities.

A friend of mine once advanced the theory that all pure substances were odorless, and that all odors were due to impurities. This theory was born of an article that harks back several years, but which is worth reviving here. It was found by Finckh² that the odor of the sulphides and mercaptans can be entirely removed by a simple process. Now the mercaptans have been known to cause public riots; and Emil Fischer once showed that 1/460, 000,000 of one milligram of ethyl mercaptan can be detected by the average unaided human nose. Yet the pure mercaptan is odorless; so that this small amount of mercaptan that Fischer smelled owed its recognition to the much smaller amount of the impurity which it contained. An interesting corollary of my friend's theory is that even this impurity is odorless in the pure state, and owes its odor to the presence of some other impurity. The subject is a promising one for investigation.

The importance of *physical chemistry* for the development of organic chemistry is increasingly manifest, and grows day by day. I need not more than refer to the use of physical constants in the determination of molecular structure; the methods and results of "spectro-chemistry," molecular-volumetric studies, thermochemical investigations, etc., are sufficiently well known. It will be sufficient to emphasize the warning that all of these methods

¹ Hesse : *Ber. d. chem. Ges.*, **32**, 2611 (1899); H. and E. Erdmann : *Ibid.*, p. 1213.

² *Ber. d. chem. Ges.*, **27**, 1239 (1894).

depend upon extrapolations the moment they are applied to new classes of compounds, and that they share with all other extrapolations the risk of running ahead of the facts. This seems notably true of the spectro-chemical studies of nitrogen compounds. Nor need I refer to the use of electrolytic conductivity for studying the dissociation of organic acids, bases and salts; these applications are sufficiently obvious.

It is in the use of the physico-chemical methods of thinking that organic chemistry will make the greatest progress. Thus, the study of reaction velocities, of the really active molecules when two or more substances are brought together, of the consequences rather than of the fact of ionization, have already made notable additions to our comprehension of organic reactions. A few examples will suffice.

Thus, Lewkowitsch was able to show by a study of reaction velocities that when fats are saponified the acid radicals attached to glycerine are separated one at a time, and not all three simultaneously.¹ Hantzsch has made continual use of electrolytic methods for tracing out the isomerization of diazo compounds (the references are too numerous to be cited). Walker has shown that the historical isomerization of ammonium cyanate to urea takes place between the ions of the salt, and is not a so-called "molecular rearrangement."² And numerous investigations of organic reactions have been carried out by H. Goldschmidt and his pupils upon a physico-chemical basis.³

The use of the electric current for oxidizing and reducing organic compounds affords another instance of the interrelation of physical and organic chemistry. The successful employment of the electric current calls for a very careful study of the electrical processes themselves, as may be seen from the recent work of Tafel.⁴ Once the details are mastered, however, excellent results can be obtained.

It is to be hoped that the time is not far distant when the word "catalysis" will vanish from the chemist's daily vocabulary. At present, it is merely a mystifying cloak to conceal our ignorance. It will be shown below that in the case of auto-oxidation the function of the catalyst is growing clearer. Meanwhile, the discovery of new catalysts, that is to say, of deeper mysteries of reaction, proceeds with unabated vigor. Michael has recently made the remarkable observation that the presence of methyl cyanide greatly increases the reaction-velocity of metallic sodium on organic compounds.⁵ Thus, methyl iodide reacts very slowly with sodium in the cold; a few drops of methyl cyanide cause the reaction to proceed almost with violence.

¹ *Ber. d. chem. Ges.*, **33**, 89 (1900).

² *J. Chem. Soc.*, **71**, 489 (1897).

³ Cf. *Ber. d. chem. Ges.*, **33**, 1140 (1900).

⁴ *Ber. d. chem. Ges.*, **33**, 2209 (1900).

⁵ *Am. Chem. J.*, **28**, 419 (1901).

The stereochemistry of carbon has made no notable progress during the last few years. A great deal of work has been done, but this has been devoted to extending our knowledge of the applications of stereochemistry rather than to enlarging our knowledge of the subject itself. In this connection, a recent utterance of Emil Fischer is of some significance.¹ He rebukes the general tendency to rush to stereochemistry as a final explanation of isomerism, and warns us to be ever mindful of its limitations and imperfections.

It is often the simplest cases of isomerism that are the hardest to explain. A simple case that *can* be explained therefore possesses a double interest. Keiser has obtained a second form of acetylene diiodide;² the best explanation is that of stereoisomerism :



We are here crowding closely upon the final explanation of the isomerism of unsaturated compounds, for the geometrical interpretation does not please everybody.³

Another observation connected with stereochemistry deserves a moment's attention. W. A. Noyes has announced that optical activity may be present in substances that do *not* contain an asymmetric carbon atom.⁴ Baeyer made a similar announcement a few years ago, and anent a very similar compound. Baeyer withdrew his announcement a few months later ; I fear the similarity will extend to the same point in the former instance. Noyes' observation is important—if true.

Buchner's discovery that alcoholic fermentation is a chemical and not a physiological process is too well known to require detailed presentation here. Suffice it to say that the numerous skeptics who assailed this discovery at its first appearance, have either been silenced or convinced. One recent interesting confirmation is worth nothing ; it is possible to kill the yeast cells completely, so that further growth and reproduction ceases ; these dead yeast cells still possess the power of fermentation.⁵ Further proof of non-vital fermentation would seem to be unnecessary ; the fact being established, the mechanism now calls for careful study.

An observation that promises to be of much significance was recently made by Gomberg.⁶ If triphenylchlormethane be treated with various metals, the halogen atom is removed, and a highly unsaturated hydrocarbon remains :

¹ *Ber. d. chem. Ges.*, **32**, 2726 (1899).

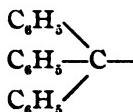
² *Am. Chem. J.*, **21**, 261 (1899).

³ Cf. Micheal : *J. prakt. Chem.*, (2), **82**, 289 (1895).

⁴ *Am. Chem. J.*, **24**, 289 (1900).

⁵ Cf. Bokorny : *Chem. Centrbl.*, (1901), **1**, p. 1207.

⁶ Cf. *Am. Chem. J.*, **28**, 315 (1901).



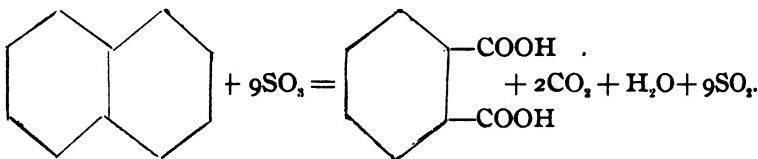
Gomberg assumes this hydrocarbon to be triphenylmethyl, and ascribes its unsaturated properties to the presence of a trivalent carbon atom. It is too early to dilate upon the consequences of this discovery ; but when the conditions which limit the existence of trivalent carbon are better known, a rather serious review of present conceptions will be inevitable.

The chemistry of naturally occurring substances, which engrosses the attention of a large number of the world's most skillful chemists, is of rather too detailed and complicated a character to be incorporated in a brief review like this. To be properly presented, the progress made in the study of the terpenes, of camphor, of caoutchouc, of starch, of cellulose, of the innumerable natural and artificial dye-stuffs, should in each case have a whole paper devoted to that one subject only ; and it seems better to omit their consideration altogether than to attempt a fragmentary and unsatisfactory jumble of facts.

The interests of the hour, however, permit of one exception to this sweeping exclusion. The chemical world has recently been stirred to the highest enthusiasm by the successful commercial synthesis of indigo. The laboratory synthesis of indigo was achieved long ago by Baeyer and others ; but the transfer of this laboratory process to the factory on a scale to permit of competition with natural indigo offered innumerable obstacles, and over twenty years of unexampled industry and intelligence were necessary before the problem was solved. Many a sermon can be preached upon this achievement as a text ; such as the examples set in patience, in foresight, in intelligent cooperation of the scientist and the technologist, in the expenditure of enormous sums for "scientific" work, etc. From the scientific side, it is a matter of chemical history that many of the modern problems and achievements took their rise in and around the investigations of indigo. H. Brunck, one of the directors of the "Badische Anilin und Soda Fabrik," has recently given an outline of the methods employed by his factory in the elaboration of their successful venture.¹ Permit me to outline the actual manufacture of indigo as it is carried out now by the Heumann process (D. R. P., 91202).

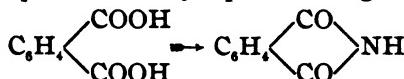
Starting with naphthalene, the cheapest and most abundant of the coal-tar ingredients, oxidation with highly concentrated sulphuric acid gives phthalic acid (and sulphur dioxide) :

¹ *Ber. d. chem. Ges.*, 33, Sonderheft, p. 71, (1900).

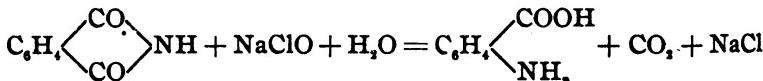


10,000 tons of naphthalene are used annually.

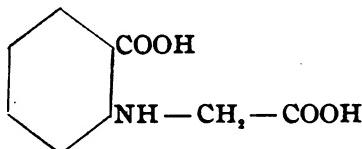
The recovery of this sulphur dioxide (some 40,000 tons annually) is an important matter; and it is interesting to note that the new "Badische" contact process is absolutely essential to the economical reconversion of sulphur dioxide into trioxide. This oxidation is accomplished by the air, so that at bottom it is the oxygen of the air that oxidizes naphthalene to phthalic acid. To give some idea of the immensity of this manufacture, even at this early stage of its development, a simple calculation shows that each year the oxygen standing over $1\frac{1}{4}$ acres of the earth's surface is completely exhausted. The phthalic acid thus obtained is converted into phthalimide by a process not given to the public:



Over 1,200,000 lbs. of ammonia are needed for the annual output. By means of sodium hypochlorite, phthalimide is converted into anthranilic acid:



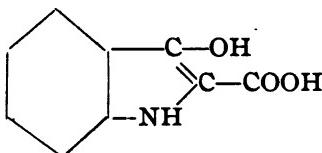
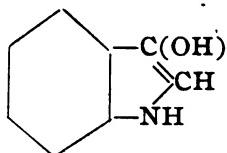
The anthranilic acid thus obtained is united with chloracetic acid, forming phenylglycocollic orthocarboxylic acid:



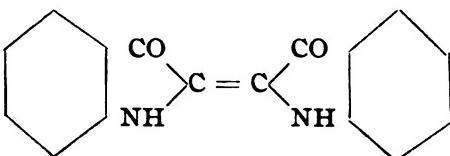
For this reaction, the "Badische" annually consumes 4,500,000 pounds of glacial acetic acid, requiring 26,000 cords of wood for their production. The chlorine needed for making chloracetic acid and anthranilic acid (above), is generated electrolytically,¹ and purified by liquefaction. 10,000,000 pounds of salt are consumed for this purpose (the contents of more than 37,000,000 gallons of sea-water, or of a cube of sea-water 368 feet on edge).

By fusing the last-named product (phenylglycocollic carboxylic acid) with caustic soda, two products may be obtained, according to conditions: indoxylic acid (I), or indoxylic acid (II):

¹ Assuming an average current yield, 9,500,000 kilowatts or a steady consumption of 350 H. P., every second of the year are required for this process.



These, when oxidized by air in presence of alkalies, pass into indigo:



The present annual production of synthetic indigo has not been given to the public, but from the data obtainable it cannot be far from 3,000,000 pounds—about one-fourth of the world's supply. It is going to be a question of business rather than of manufacture when the indigo factories will have supplanted the indigo fields. Some of the above calculations will give a faint idea of the purely commercial side of this stupendous undertaking. The "Badische" has already invested over \$4,500,000 in the plant and preliminary experiments.

THE NEW ORGANIC CHEMISTRY.

The investigations we have just passed in rapid review have this in common, that they belong to the established order of things, and offer novelty chiefly in facts, hardly at all in principle. There is a newer organic chemistry in the air, however, just as there are a newer inorganic and a newer physical chemistry; and the developments of the newer organic chemistry are likely to be as startling as those of the older branches. The new organic chemistry at present tends in two directions, both of which shall engage our attention for a few minutes. The one is comprehended under the phenomena of tautomerism; the other deals with the chemistry of those elements other than carbon which enter into organic compounds.

Tautomerism and its allied phenomena constitute one of the most difficult subjects of experimental science. Perhaps it will be best to give first of all a résumé of the nomenclature adopted by most of the investigators concerned in this work. By tautomerism in general, chemists have been accustomed to mean the ability of a single substance to behave as if it had two or more different structures, or to give derivatives belonging in two or more different classes. The closer investigation of these cases has

shown that a much more careful method of classifying the facts is necessary.¹

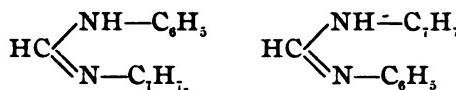
When two or more substances exist, so closely related that they pass into each other spontaneously, or upon very slight provocation (stereoisomerism being excluded), we speak of desmotropy; *e. g.*, dibenzoylacetyl methane, which forms the desmotropic isomers:²



If we have two sets of derivatives, but only one mother-substance extant in the free state, we have a case of tautomerism proper; *e. g.*, hydrocyanic acid, from which we can obtain two distinct series of esters:

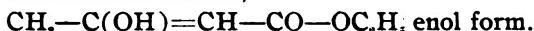


A similar tautomerism exists in the case of the amidines; *e. g.*, phenyltolyl formamidine, which behaves as if it possessed both of the following formulas:

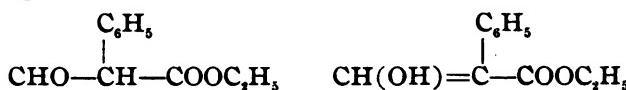


Such a case, where both tautomeric forms possess identical chemical character, is described as virtual tautomerism. Functional tautomerism exists where the (two) forms have different chemical character, as with acetoacetic ester; this reacts as a ketone,

$\text{CH}_3-\text{CO}-\text{CH}_2-\text{CO}-\text{OC}_2\text{H}_5$ keto form,
and as an unsaturated alcohol,



Desmotropic isomers tend to change into each other upon fusion, upon solution, in various solvents, etc.; in nearly all instances, a condition of equilibrium is finally reached, when we have the isomers present at the same time. This condition is known as allelotropy. An example is found in Wislicenus' phenylformylacetic ether, which upon solution in alcohol or in chloroform forms an allelotropic mixture of the two forms:

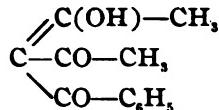


It sometimes happens that of a pair of desmotropic substances, the conditions of equilibrium are such that one can exist only in

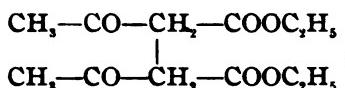
¹ Cf. Rabe: *Ann. Chem. (Liebig)*, 313, 129 (1900).

² Cf. Claisen: *Ibid.*, 201, 25 (1896).

traces ; this limiting case of desmotropy is called pseudomerism ; e. g., benzoyldiacetyl methane:¹



The investigation and definition of substances in this category is an exceedingly tedious and difficult affair. Without going into details, one citation will suffice. Diacetosuccinic ester,

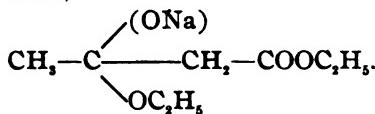


can exist in no less than thirteen different forms, of which Knorr has already described five.²

The question of tautomerism calls to mind the old battle-ground of acetoacetic ether. I have no desire to open old wounds, and so will cite only one publication dealing with this vexed question. Michael disagrees with Claisen's commonly accepted theory of the synthesis of acetoacetic ether (the addition of sodium ethylate to acetic ether, with subsequent condensation and elimination of alcohol), because metallic sodium acts upon acetic ether so much better than sodium ethylate. Michael thinks the primary formation of sodium acetic ether much more probable,³



This unsaturated compound then adds a molecule of unchanged acetic ester,



We cannot do more than refer to the tautomerism of the acid amides⁴



and to that of the oxyazo compounds, which seem to be either phenols or quinone-hydrazone according to circumstances.⁵ In these cases, as in many others, two general rules must ever be kept in mind : One that generalizations are misleading, and that each case must be investigated upon its own merits,⁶ the

¹ Cf. Knorr: *Ann. Chem. (Liebig)*, **306**, 350 (1899).

² *Ibid.*, **306**, 332 (1899).

³ Cf. *Ber. d. chem. Ges.*, **33**, 3731 (1900).

⁴ Cf. Titherley: *J. Chem. Soc.*, **79**, 391 (1901).

⁵ Cf. McPherson: *Am. Chem. J.*, **25**, 485 (1901).

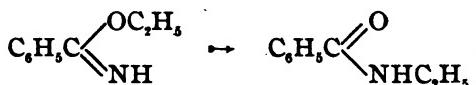
⁶ Cf. Claisen: *Ann. Chem. (Liebig)*, **291**, 45 (1896).

other that the metal derivatives (salts) of tautomeric and desmotropic forms are almost always constituted with their metal attached to oxygen when that is possible. This latter rule, laid down by Michael, was formally approved by no less an authority than Baeyer a short time ago.¹

This theory of Michael's was recently elaborated and developed by Hantzsch, in connection with the latter's investigation of the diazo compounds.² In order to determine which of the two possible structures a tautomeric compound may have, Hantzsch shows that if one form may be acid in character the diagnosis is easy. If the given substance have the acid formula, it will be an electrolyte, and will form salts instantaneously; if it possess the neutral formula, it will (usually) be a non-conductor, and it forms salts with measurable velocity. It was this theory that led Hantzsch to revise his erstwhile views of the isodiazo compounds.³

Differing from tautomerism in outward appearance, yet closely related in their internal mechanism, are those reactions for which we possess no good English name. The Germans call them "Umlagerungen;" we are obliged to use the much more awkward term "molecular rearrangements." Fittig has long been engaged in studying the rearrangements occurring in unsaturated acids. The double bond in these acids seems to migrate from one part of the molecule under conditions that do not admit of prophecy,⁴ so that in spite of the enormous amount of labor devoted to this investigation by Fittig and his pupils, no reliable generalizations can be drawn of the behavior of these substances.

Interesting rearrangements have been studied by H. L. Wheeler and his pupils.⁵ These deal with the changes occurring in various acid amide derivatives. To cite only one example, phenylformimido ether is easily isomerized into ethyl benzamide,



Time will not permit of more than a reference to Bamberger's study of the rearrangements of aromatic nitrogen compounds; *e. g.*, phenylhydroxylamine⁶ forms a complex mixture of products on treatment with acids or alkalies. Bamberger assumes the intermediate existence of compounds with univalent nitrogen.

The second phase of the new organic chemistry is still in its beginnings. While the chemistry of carbon in its organic derivatives is by no means exhausted, an ever-increasing army of in-

¹ *Ber. d. chem. Ges.*, 33, Sonderheft, p. 64 (1900).

² Cf. above.

³ Cf. *Ber. d. chem. Ges.*, 32, 575 (1899).

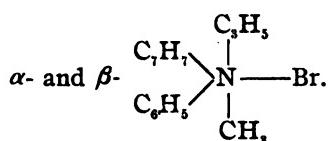
⁴ *Ann. Chem. (Liebig)*, 304, 117 (1899).

⁵ *Am. Chem. J.*, 23, 135 (1900).

⁶ *Ber. d. chem. Ges.*, 33, 3600 (1900).

vestigators is devoting itself to the study of the other elements which enter into organic compounds. To be sure, we have long been aware of the development of "nitrogen chemistry," but the peculiarities of nitrogen in its numerous compounds have been so intimately bound up with the history and progress of carbon chemistry proper, that we have not been conscious of any sharp line of demarcation. But now that we are beginning to be interested in the welfare of the carbon derivatives of other elements, the time seems ripe for a systematic attempt to "organize" inorganic chemistry; *i. e.*, to study the inorganic elements as carbon has been studied. Much valuable material has already been collected for this purpose.

During the past year or two, much interest has been accorded the stereochemistry of other elements. It is hardly necessary to recall the tremendous influence that the theories of van't Hoff and LeBel have had on the growth of carbon chemistry during the past twenty years. LeBel himself extended his studies to nitrogen, and had succeeded in obtaining an asymmetric nitrogen compound possessing optical activity.¹ To be sure, there was considerable skepticism about LeBel's results, until he showed that the greatest care is necessary in separating the optical isomers by fermentation, the method he had adopted. How quickly our views on such things change! Only two years ago Marckwald published some work to prove conclusively that these so-called isomers could not be separated.² To-day a dozen groups of isomers have been carefully studied. There was needed only the proper reagent. This was found by W. J. Pope in camphor sulphonate acid, $C_{10}H_{16}O.SO_3H$.³ A short time before, Wedekind⁴ had prepared two isomeric forms of a substituted ammonium salt; *viz.*, benzylphenylallylmethyl ammonium bromide (and iodide),



These isomers were inactive. Pope succeeded in separating the α -form into two optically active modifications, turning polarized light to the right and to the left almost equally ($[\alpha]_D + 68.6^\circ$ and -67.3°). Pope has since then prepared numerous other active ammonium compounds.

The sulphur atom also has the power of becoming asymmetric. Pope and Peachey⁵ have isolated an optically active *d*-methyl-

¹ *Compt. rend.*, **112**, 724 (1891).

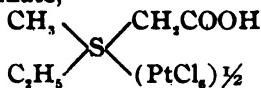
² *Ber. d. chem. Ges.*, **32**, 560 (1899).

³ *J. Chem. Soc.*, **78**, 1127 (1900).

⁴ *Ber. d. chem. Ges.*, **32**, 517 (1899).

⁵ *Loc. cit.*, p. 1072.

ethylthetin chlorplatinate,



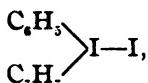
The asymmetric sulphur atom is easily racemized; *i. e.*, rendered inactive by isomerization of half the molecules present.

Tin, an element resembling carbon and sulphur in that it can become quadrivalent, may also be rendered asymmetric and optically active.¹ Methyleneethylpropyl stannic iodide,



is an oil, and is dextrorotatory. The chief peculiarity of this asymmetric tin atom, however, is that no laevorotatory modification exists. As fast as the dextro form separates, the remaining laevo racemizes itself, thus forming fresh dextro, which alone separates. By completely evaporating the solution to dryness, the whole of the previously inactive salt is converted into its dextrorotatory isomer. This fact is of great significance for the future of stereochemistry.

Efforts to render the iodine atom in iodonium compounds asymmetric have proved abortive so far.² Phenyltolyliodonium iodide,



could not be rendered optically active.

It is to be expected that molecular asymmetry will be discovered in a great many other elements. Numerous elements are capable of combining with carbon radicals, and many curious compounds have resulted. We cannot do more at this time than refer to the extensive studies that Michaelis has been carrying on for years with the organic derivatives of selenium, tellurium, phosphorus, boron, silicon, etc. Michaelis has recently told us his motive in this work. He points out³ that the type theory, to which organic chemistry has owed so much of her early progress, has been deserted by the modern "organiker." His own work has been carried on for the express purpose of developing this theory, which he hopes will eventually lead to an insight into the real laws of combination.

Quite a number of new mercury compounds of organic radicals have been prepared recently, a number of investigators apparently stumbling upon them at about the same time. Thus, Dimroth⁴ has found that aromatic compounds generally easily replace

¹ Proc. Chem. Soc., 16, 42 (1900).

² Kipping and Peters: Proc. Chem. Soc., 16, 62 (1900).

³ Ann. Chem. (Liebig), 314, 276 (1901).

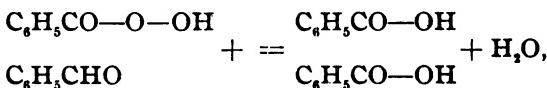
⁴ Ber. d. chem. Ges., 31, 2154 (1898); 32, 758 (1899).

one or more hydrogen atoms by univalent mercury radicals; a different class of aromatic quicksilver compounds related to benzoic acid are described by Pesci;¹ whereas Hofmann and his pupils² have found that in the fatty series four different types of substitution of mercury for hydrogen can be distinguished.

Even the chemistry of so well-known an element as oxygen has been greatly extended by the organic chemist within the last few years. One important topic, though outside the lines of organic chemistry proper, may be alluded to. The phenomena of auto-oxidation have excited much interest. Many substances which are absolutely indifferent towards free oxygen (moist or dry) are easily oxidized in the presence of certain other substances. In many instances, these "contact-substances" or catalysts are themselves oxidized at the same time. In other cases, they remain unchanged. The exact mechanism of auto-oxidation still needs very careful study, in which Manchot³ has made an excellent beginning. Hydrogen peroxide often plays an important part in these reactions as an intermediate product. In other cases, again, Baeyer and Villiger have been able to demonstrate the intermediate formation of complex organic hyperoxides;⁴ thus benzaldehyde, which in moist air is oxidized to benzoic acid, first takes up a molecule of oxygen, forming benzoyl hydroperoxide,



This will oxidize a second molecule of benzaldehyde,



but other substances are usually oxidized first if they are present.

Baeyer and Villiger have also prepared mono- and diethyl-hydrogen peroxide. The former, preferably called ethyl hydrogen peroxide, is easily prepared by action of hydrogen peroxide upon ethyl sulphate. It has the formula $\text{C}_2\text{H}_5 - \text{O} - \text{OH}$, is fairly stable, and differs from its mother-substance hydrogen peroxide (now called hydroperoxide) in possessing no reducing properties whatever; it is merely an oxidizing agent.⁵

The same chemists obtained diethyl-peroxide from the same reagents in different proportions. It has the formula $\text{C}_2\text{H}_5 - \text{O} - \text{O} - \text{C}_2\text{H}_5$; it has neither oxidizing nor reducing properties. Reducing agents convert it into alcohol. From the behavior of these two compounds Baeyer thinks that hydrogen peroxide itself has the old formula $\text{HO} - \text{OH}$; the existence of

¹ *Atti dei Lincei Roma*, (5), 9, 255 (1900).

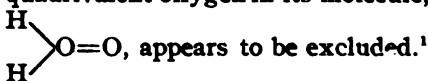
² Cf. *Ber. d. chem. Ges.*, 33, 1328-1364.

Cf. *Ztschr. anorg. Chem.*, 27, 397 (1901).

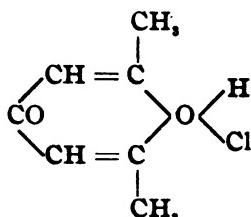
⁴ *Ber. d. chem. Ges.*, 33, 1581 (1900).

⁵ *Ibid.*, 34, 738 (1901).

quadrivalent oxygen in its molecule, as in the suggested formula



But although hydroperoxide may not contain quadrivalent oxygen, the fact that oxygen does become quadrivalent in some of its compounds has been established by Collie and Tickle.² Dimethyl-pyrone forms salts with various hal-hydric acids; e. g., the hydrochlorate



These salts behave like the salts of a very weak base, and are completely hydrolyzed in dilute aqueous solution. If the addition of hydrochloric acid had occurred within the carbon ring, this hydrolysis would not manifest itself.

Oxygen owes its name to its strong acid-forming tendencies. We should expect that as we increase the amount of oxygen in a given molecule, the acid properties of that molecule would show a proportional augmentation. But such does not seem to be the case. If in benzoic acid, $\text{C}_6\text{H}_5\text{CO}-\text{OH}$, we introduce a third oxygen atom in the place where it ought to have the greatest acidifying influence (*viz.*, in the carboxyl group itself, $\text{C}_6\text{H}_5\text{CO}-\text{O}-\text{OH}$), the resulting compound (benzoyl hydroperoxide) is not only less acid than benzoic acid, but is actually weaker than carbonic acid.³ It would have been difficult to foresee this.

SOME NEW ORGANIC THEORIES.

Time and space will not permit more than a brief reference to the recent endeavors to extend our fundamental conceptions of organic processes. For many years, chemists have been content to study organic chemistry with attention fixed chiefly upon matters of detail. The larger aspects of the subject have lain dormant until quite recently. During the last few years, however, an effort has been made on several sides to replace some of our theoretical views by others better suited to present conditions. For it must not be concealed that many investigators are dissatisfied with structural and with stereochemical methods of explana-

¹ Ber. d. chem. Ges., 33, 3392 (1900).

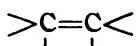
² J. Chem. Soc., 75, 710 (1899).

³ Baeyer-Villiger: Ber. d. chem. Ges., 33, 1569 (1900).

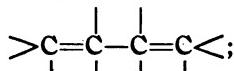
tion, dissatisfied with the idea of valence, aye, even with the atomic theory itself.¹

In the nature of things, all recent and untried theories meet with opposition ; they are often crude in detail, sometimes in error as to facts ; and for our present purposes it will be better to sketch in a few words what the theorists are hoping to achieve rather than attempt to weigh what they have actually accomplished. Organic chemistry is in no urgent need of new guide-posts (witness the mass of new material each year), so that our caution is at least pardonable.

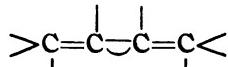
A comprehensive theory of unsaturated compounds has been attempted by Thiele.² His fundamental idea is that in the so-called double bond the carbon atoms are really united by two valence units each, but that a small amount of "residual affinity" is left :



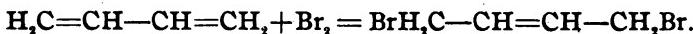
It is this residual affinity that gives to the double bond its additive power ; as addition occurs, more residual affinity is liberated, owing to a sort of equilibrium condition. In the case of two adjacent double bonds, two pairs of residual affinities would exist,



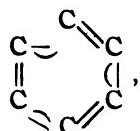
but the central pair neutralize each other, just as two magnet bars would, and we have residual affinity left only at the extreme ends of such a "conjugated system of double bonds" as Thiele calls it :



In this way he seeks to explain the actual fact that where such a pair of double bonds occurs within a molecule, addition takes place only at the outer ends, with the establishment of a new double bond :



Applied to benzene, this theory shows us three conjugated double bonds,



and many of the peculiarities of benzene can be brought into rela-

¹ Cf. Ostwald's "Text-book of Inorganic Chemistry."

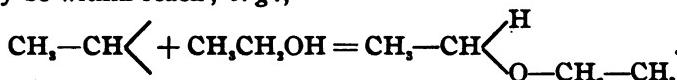
² Ann. Chem. (Liebig), 306, 87 (1899).

tion to the properties of other unsaturated compounds. Thiele has found a supporter in Baeyer,¹ who declares that here we have the "final expression" of thirty years of discussion. As we owe the bulk of our knowledge of the benzene ring to Baeyer, this sounds encouraging.

An entirely different method of explaining organic reactions and additions has been elaborated by Nef;² according to him, organic compounds have an irresistible tendency to become strongly unsaturated, with formation of bivalent carbon; *e. g.*,



and an equally irresistible tendency to pass back again to the saturated, quadrivalent condition by adding on any molecules that may be within reach; *e. g.*,



What is missed in Nef's theory is the motive; it is often difficult to see why some other form of addition does not occur when a number of different, available molecules are present. Nef's views have not found the support that has been accorded to Thiele's theory.

Finally, a third course of reasoning has been developed by Michael.³ Michael's theory is too recent, too complicated and too extensive to permit of any properly comprehensive summary. In its essence, it ascribes to every atom in the molecule a polarity (which is expressed in electric terms); addition reactions are caused by attempts to neutralize this polarity; and the polarity of each atom is modified more or less profoundly by the presence and polarity of all the other atoms in the molecule. With reference to the theories of Thiele and Nef, Michael endeavors to show that Nef's views do not agree with the facts, whereas all of Thiele's deductions can be drawn from his own,—these being more general and more fundamental. If I may append my personal opinion of these three theories, I should venture the prediction that Michael's is more likely to grow into the needs of organic chemistry than either of the others.

CONCLUSION.

It will be seen that the prospects of organic chemistry are as bright as ever. At each of the older problems hosts of busy workers are successfully laboring. New problems are constantly arising, and new methods of experimentation are being as steadily devised for their study. A healthy and skeptical criticism is being accorded our present theories; and from the constructive side

¹ *Ber. d. chem. Ges.*, 33, Sonderheft, p. 63 (1900).

² *Ann. Chem. (Liebig)*, 298, 202 (1897).

³ *J. prakt. Chem.*, 60, pp. 1-178 (1899).

efforts are not lacking to provide us with more accurate and more comprehensive generalizations. From within and without, the organic chemist is stimulated to his best endeavors; his efforts are encouraged, and his achievements are appreciated. The scientist can ask no more.

To him, however, busy with other work, who gazes occasionally on organic chemistry, it may often seem to lack coherence of effort, to waste its strength burrowing for details, and to owe many of its successes to mere chance. If such a one there be, I recommend to his attention a notable address by Baeyer last year.¹ From this address he will learn of the unity of research work—that nearly all of this master's brilliant discoveries were due not to luck or chance, but to the consistent prosecution of a logical train of ideas. Baeyer's first extensive research work dealt with uric acid. The similarity of alloxan and isatin led him to the indigo group. From this sprang the tension theory, the quinoline synthesis, and tautomerism. The tension theory led to the curious tetra-acetylene dicarboxylic acid; this to the benzene ring studies. The investigation of terpenes and related substances took its rise from their similarity to reduction products of benzene. During the terpene researches some curious peroxides were obtained, and the work described above (on ethyl hydroperoxide, etc.) resulted from following up these latter. Thus we can trace Baeyer's research work—than whom no single man has contributed more to the stupendous growth of organic chemistry—back in an unbroken logical chain extending over forty years.

There lies here a world of thought for him who cares to find it.

ARTHUR LACHMAN.

NOTE.

A Gravimetric Method for the Estimation of Hydrogen Dioxide.

—All the methods thus far described for the estimation of hydrogen dioxide are volumetric, which may be divided into the three following classes: first, gasometry, by the use of Lunge's nitrometer, or some modification of it; second, iodometry, originated by Kingzett, and depends upon the liberation of iodine from potassium iodide in the presence of sulphuric acid; and, third, oxidimetry, the mutual decomposition of potassium permanganate and hydrogen dioxide in the presence of sulphuric acid. Of these three methods, the latter is preferred and most frequently used. The author has obtained good results by estimating the hydrogen dioxide as water. For the purpose a "Schrötter" apparatus (with tube and glass stoppers), such as used for carbon

¹ *Ber. d. chem. Ges.*, 33, Sonderheft, p. 52ff. (1900).

dioxide determinations in mineral carbonates, was employed. The drying tube was half filled with concentrated sulphuric acid and the "acid tube" with a solution of potassium permanganate (2 grams in 100 cc. water). The bulb contained 10 cc. water and 5 cc. of dilute sulphuric acid (1 : 5). The weight of the apparatus was now noted and then about 1 cc. of the hydrogen dioxide was introduced. The apparatus was again weighed to insure the amount of hydrogen dioxide added. The permanganate was now allowed to flow in drop by drop until a permanent faint rose tint was formed. The apparatus was next allowed to cool and then weighed. The author claims that if the usual precautions are exercised, as prescribed in carbon dioxide determinations, excellent results can be obtained. However, it must be remembered that the loss in weight must be divided by 2, because one-half of the oxygen comes from the permanganate itself, and, furthermore, a too great excess of the latter must be avoided because the sulphuric acid decomposes it, giving off oxygen, thus leading to higher results.

GEORGE E. HOSCH.

NEW BOOKS.

JAHRBUCH DES VEREINS DER SPIRITUS-FABRIKANTEN IN DEUTSCHLAND.
Erster Band, 1901. Berlin: Paul Parey. 316 pp. Price, 6 M.

This volume gives reports of the work of the German Society of Alcohol Distillers, also of the Society of Starch Manufacturers, for 1900 and is the first of the series. Heretofore the minutes and reports of these organizations have been published in the form of a supplement number to the *Zeitschrift für Spiritusindustrie*. This first volume of the new yearbook contains 316 pages and presents not only the proceedings of the two societies but also a large amount of statistical matter relating to production and consumption of alcohol and starch. The first-named society supports a number of experimental laboratories, and the investigations of these are briefly described in the book. As alcohol may be used in the arts in Germany tax-free under certain restrictions, space is devoted to a discussion of new outlets for alcohol in various directions. The chapter relating to the advantages of the alcohol motor presents some very interesting data and is one of the best in the book.

J. H. LONG.

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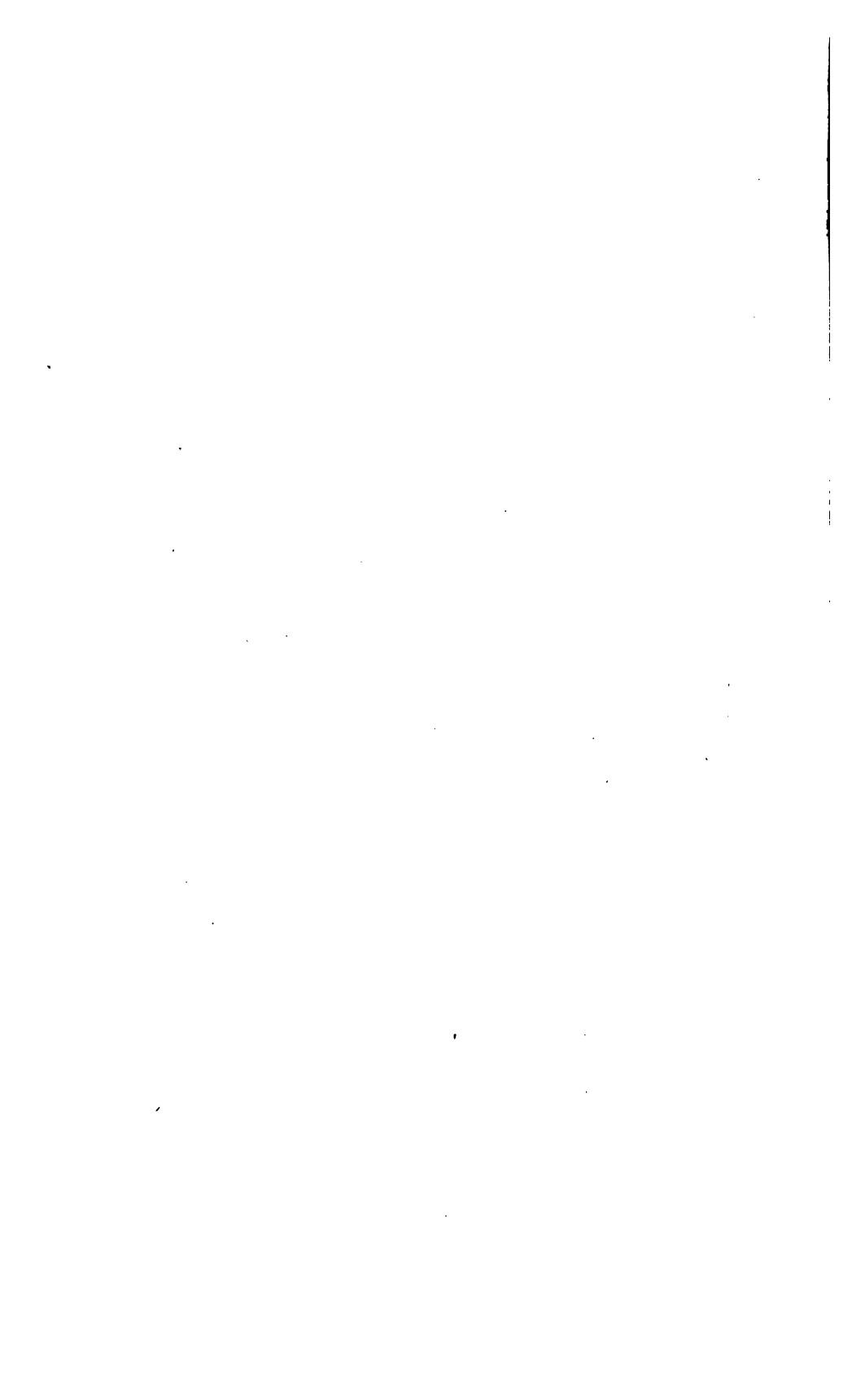
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Taylor, Thomas M., 211 N. Professor St., Oberlin, Ohio.
Thatcher, R. W., Pullman, Wash.
Von Egloffstein, C., 58 Garden St., Brooklyn, N. Y.

MEETINGS OF THE SECTIONS.

PHILADELPHIA SECTION.

The annual meeting of the Philadelphia Section of the American Chemical Society was held in Philadelphia, May 16, 1901.

The meeting was called to order in the Harrison Laboratory, University of Pennsylvania, at 8.15 P.M., Dr. Jayne in the chair. There were twenty-five members and visitors present.

The minutes of the previous meeting were read and approved.

The following were nominated to fill the various offices for the ensuing year :

Presiding Officer.—J. Merritt Matthews.

Secretary and Treasurer.—F. E. Dodge.

Executive Committee.—O. L. Shinn, R. H. Bradbury, E. Schlichting.

There being no further nominations, on motion of Dr. Leffman, the secretary was instructed to cast one ballot for the nominees. The ballot was cast, and the nominees were declared elected.

It was moved and seconded that a written notice, advising that the proposed change in the by-laws,—electing a vice-chairman for the same term and at the same time as the other officers of the section,—be sent to each member of the section ; the motion was carried.

The paper of the evening was " Some Investigations upon the Interaction of Carboxyl and Cyanogen Compounds," by Marston Taylor Bogert, of Columbia University.

The paper was discussed by Dr. Leffmann and others.

There being no further business the meeting adjourned at 9.30.

F. E. DODGE, *Secretary*.

Issued with August Number, 1901.

Proceedings.

COUNCIL.

NAMES PROPOSED FOR MEMBERSHIP.

Hosch, George E., 904 St. John's Place, Brooklyn, N. Y.
Lyon, A. E., care Chiapos Mining Co., Teapa, Tabascos, Mex.
Pegg, E. F., 100 W. Clinton St., Cleveland, Ohio.
Potter, Nathan S., Jr., Cement City, Mich.
Schlundt, Herman, Madison, Wis.
Stuart, Duncan, 1937 13th St., N. W., Washington, D. C.
Wells, J. Walter, Provincial Assay Office, Belleville, Ont.

NAME PROPOSED FOR ASSOCIATE MEMBERSHIP.

Kimball, Sherman, Palo Alto, Cal.

CHANGES OF ADDRESS.

Atwood, Frank W., 20 Central Wharf, Boston, Mass.
Fox, C. B., 257 Main St., East Hamilton, Canada.
Huntington, Harwood, University Club, 1 W. 54th St., New York City.
Laws, E. H., Box 157, Bedford, Mass.
Leach, Mary F., 74 Pitcher St., Detroit, Mich.
Morgan, Wm. Conger, Univ. of Cal., Berkeley, Cal.
Roberts, Alfred E., Wethersfield, Conn.
Root, Wm. L., 11 Church St., Pittsfield, Mass.
Ryland, Garnett, Richmond College, Richmond, Va.
Saunders, A. P., Hamilton College, Clinton, N. Y.
Wagner, Theodore B., 697 N. Robey St., Chicago, Ill.

ADDRESSES WANTED.

Boroscheck, Leopold, formerly of 149 E. 56th St., N. Y. City.
Niese, H. E., formerly of Matthiesen & Wiechers, Jersey City,
N. J.
Waters, C. D., formerly of 6 Magnolia St., Roxbury, Mass.

MEETINGS OF THE SECTIONS.

KANSAS CITY SECTION.

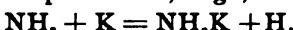
The first regular meeting was held on January 8, 1901, in the

rooms of the Kansas City College of Pharmacy, 714 Wyandotte street, Professor Bailey, of Kansas University, presiding.

The report of the Executive Committee on By-Laws was read and accepted.

Professor E. C. Franklin, of Kansas University, gave a talk, illustrated by experiments, on the subject, "Ammonia, A New Electrolytic Solvent."

Professor Franklin at first reviewed briefly the general properties of gases and of solution. He then performed some experiments with liquid ammonia. He showed its action as a solvent upon a number of substances. He called special attention to the analogy between liquid ammonia, in all of its reactions, and water. For example, it is acted upon by the alkali metals to form compounds analogous to the hydroxides formed by the action of these metals upon water; *e.g.*,



These compounds are neutralized by acid amides just as bases are neutralized by acids. Phenolphthalein may be used to indicate the neutral point, as can also many others of the usual indicators. Litmus is insoluble.

Professor Franklin also explained briefly the apparatus, practically all of which was made by himself, used for purifying the commercial liquid. He also explained the apparatus and methods used for determining its physical constants.

A motion was passed to give Professor Franklin a vote of thanks for his interesting talk.

The meeting then adjourned.

The second regular meeting was held at 714 Wyandotte St., February 12, 1901, Professor Bailey presiding.

Mr. Chas. Van Brunt, one of the chemists for the American Smelting and Refining Co's plant at Argentine, Kansas, read an interesting paper on the subject, "The Electrolytic Determination and Separation of Antimony."

After reviewing the gravimetric methods, given in textbooks, for the determination of antimony, and the volumetric method of Kessler, he took up the electrolytic method of precipitation from alkaline sulphide solution.

Mr. Van Brunt said in part :

The unmodified method of Classeu has some serious drawbacks, the difficulty being chiefly due to the formation of a polysulphide, which hinders the reduction of the antimony and even

causes a re-solution of it if it is allowed to become sufficiently concentrated.

The trouble in part remedies itself by the action of the sodium and hydrogen set free at the cathode. They combine with part of the sulphur in the polysulphide, forming sodium hydrosulphide, NaHS, and reducing the polysulphide to normal sulphide. The sodium hydrosulphide, too, reacts with the sodium hydroxide formed at the cathode and re-forms the normal sulphide, Na₂S. Hence, there really will be a point at which the reduction of the antimony is complete. This is very difficult to strike, however.

Classen has suggested the use of hydrogen peroxide to destroy the polysulphide, but it cannot be used to prevent its formation.

Ost encloses the cathode and the antimony solution in a porous cell, thus keeping the polysulphide out of the way. There are a number of objections to this method, however.

It occurred to the writer that there might be some substance which would prevent the formation of the polysulphide. Potassium cyanide was tried, with entire success. The potassium cyanide combines with the sulphur to form potassium thiocyanide, which has no injurious effect. The current strength remains uniform and the deposition takes place evenly. Enough potassium cyanide is added to allow complete precipitation of the antimony before the solution turns yellow.

Alkaline salts which may have accumulated in the preceding chemical operations, do not interfere. Hydrogen peroxide is added to the antimony solution before the addition of potassium cyanide, to oxidize arsenic from the arsenious to the arsenic form, in which condition it does not interfere. The cyanide is then added in the proper amount, the solution heated, and the electrolysis performed.

A motion was passed that Mr. Van Brunt's paper be accepted and a copy of it preserved with the Society records and that Mr. Van Brunt be given the thanks of the Society.

A motion to adjourn was passed.

The third regular meeting was held at 714 Wyandotte St., March 12, 1901, with Professor E. H. S. Bailey in the chair.

Dr. Moechel, the councilor, made a report on the progress of the movement in favor of printing abstracts in the Journal.

Professor Bartow moved that the councilor be instructed that it is the sense of the section that we favor the printing of abstracts. The motion was seconded and passed.

It was decided to hold the May meeting at Lawrence, Kansas. Professor Edward Bartow, of the University of Kansas, read a

paper entitled "Some Modifications of the Friedel-Crafts Reaction."

After carefully explaining the use of aluminum chloride in bringing about the substitution of hydrogen by open-chain radicals in general, Professor Bartow spoke of his work with triphenylmethane and its derivatives. This compound may be made by the action of chloroform on benzene in the presence of aluminum chloride. The usual method of preparing it is to make the aluminum chloride either by the action of hydrochloric acid or aluminum, or by the direct combination of chlorine and aluminum, and then treating the mixture of chloroform and benzene with the prepared aluminum chloride. Professor Bartow's modification consists in treating a mixture of chloroform and benzene, having finely divided metallic aluminum suspended in it, with dry chlorine gas.

The method is entirely successful and Professor Bartow is continuing the work in this direction.

A motion was passed to thank Mr. Bartow for his paper and to file it with the records of the Society.

Dr. Moeschel brought up the question of having a bureau of information in the Journal of the Society. A motion was passed to consider this question at the next meeting.

The fourth regular meeting of the section was held at 714 Wyandotte street, April 9, 1901, Professor Bailey presiding. The minutes of the March meeting were read and approved.

The secretary reported that, upon the advice of the Executive Committee, \$15.00 had been sent to Professor Long, the chairman of the Finance Committee of the anniversary meeting.

Mr. Ottokar Hofmann, superintendent of the blue vitriol department of the American Smelting and Refining Company's plant at Argentine, presented a very interesting paper on the subject, "A New Method for Making Blue Vitriol," in which he described the ingenious process, of his own invention, now in use at the Argentine plant.

In Mr. Hofmann's process, the material, a lead copper matte, containing about 40 per cent. copper and 12 to 14 per cent. lead, is at first pulverized in a Krupp ball mill so that it will pass through a 50-mesh sieve and is then roasted in specially constructed double-story Pearce turret roasters.

The important points to be gained in this roasting are as follows:

1. To convert as much as possible of the copper sulphide to copper sulphate.

2. To convert the balance into cupric oxide, which dissolves in dilute sulphuric acid.

3. To convert the iron into the red oxide, which is only slightly soluble in dilute sulphuric acid.

This requires great skill, for a pretty high heat is necessary to convert the iron into the desired form and, at the same time, a too high temperature will decompose some of the copper sulphate, leaving cuprous oxide, in which form only half the copper will be converted into copper sulphate by the action of dilute sulphuric acid.

After roasting and again pulverizing, the material is placed in wooden tanks 12 feet in diameter and 6 feet deep, containing sulphuric acid of 2 or 3 per cent. strength.

The whole is stirred and is kept hot by steam until the solution becomes nearly neutral.

The pulp is now forced through a filter by means of a pressure tank. The crude neutral copper sulphate solution is now refined by adding some roasted matte and passing air and steam through it. This is performed in towers 9 feet in diameter and 16 feet deep, made of California redwood. Each tower is capable of handling 15,000 gallons per day and there are eight of them at the Argentine works. The copper oxide of the matte and the oxygen of the air act upon the ferrous sulphate, converting it into the red oxide and forming copper sulphate.

When all the impurities have been precipitated, the solution is again filtered.

The purified solution is now concentrated in an apparatus of Mr. Hofmann's invention, for which a patent is now pending.

The hot, concentrated solution is run into crystallizing tanks, of which there are 112 at Argentine, each with a capacity of 720 cubic feet, made of concrete.

Here the solution stands for seven or eight days, in the course of which the blue vitriol crystallizes out on strips of lead suspended in the solution. These clusters of crystals are then removed, crushed, screened, washed, dried in centrifugal machines and removed to the storage bins of the warehouse. The works produce 60 tons per day.

A motion was passed to thank Mr. Hofmann and request him to give his paper to be preserved with the records of the Society.

A motion was passed to express to the parent Society the suggestion that a query column be established in the Journal.

The Society adjourned.

The fifth regular meeting of the section was held in the Physics Building of Kansas University, at Lawrence, Kansas, May 14, 1901, with Professor Bailey in the chair.

The minutes of the April meeting were read and approved.

A motion was passed to take a vote on the question as to whether $O = 16$ or $H = 1$ should be taken as the standard of atomic weights. The vote was unanimous in favor of $O = 16$.

A motion was passed to have the June meeting of a social nature.

Professor Knerr, of Atchison, Kansas, then read a paper on the subject, "Cosmo-Chemistry."

In this paper, Professor Knerr offers a theory of chemical affinity, based upon the properties of the ether. In his opinion, chemical affinity is but a manifestation of gravity, and he attempts to explain both by his theory of the ether.

He regards the ether as made up of minute discreet particles, smaller than any of the atoms of chemistry, which he calls "protatoms," for he regards them as the foundation stuff of the atom. These protatoms are not in contact, and the spaces between them are utterly void of matter, so that they are free to move with undiminished resultant velocities, for they are perfectly elastic. So we may regard the ether as made up of protatoms, in continual motion in every direction, unhindered in the void space, save as they collide, rebound, collide again and rebound eternally. In such a chaotic condition there would arise of necessity groups of protatoms, here and there of greater or less number. Two such groups in close proximity would shield each other more or less, from external impacts of other protatoms on their adjacent paces, with the result that they would be driven closer. The energy of their own internal impacts would thus be conserved; and two such groups would constitute a molecule, in which each group would be an atom. This condition of being driven together is chemism and the energy of this external driving together is chemical affinity. In this way I would correlate gravity and chemical affinity.

After an animated discussion of the paper, and after passing a motion to thank Professor Knerr and ask him to leave his paper to be filed with the records of the Society, the Society adjourned.

Issued with September Number, 1901.

Proceedings.

COUNCIL.

NEW MEMBERS ELECTED JULY 29, 1901.

Aspinwall, Henry C., Pompton Lakes, N. J.
Bjerregaard, August P., Debevoise Ave. corner Bullion St.,
Brooklyn, N. Y.
Henwood, Abraham, Drexel Inst., Philadelphia, Pa.
Reynolds, Albert A., Williamstown, Mass.

NEW MEMBERS ELECTED AUGUST 12, 1901.

Abells, Harry D., Morgan Park, Ill.
Abrahams, Sampson, 104 Gilpin Pl., Chicago, Ill.
Brooks, Ralph O., 404 Atlantic Ave., Boston, Mass.
De Blois, W. H., Capelton, P. Q., Canada.
Jefferson, Alice M., 4062 Irving St., Philadelphia, Pa.
Kahlbaum, Geo. W. A., Univ. of Basel, Switzerland.
Ransom, Arthur McB., 156 W. Baker St., Atlanta, Ga.
Schwartz, David, Southern Cotton Oil Co., New Orleans, La.

ASSOCIATE ELECTED AUGUST 12, 1901.

Pritchard, Fred., 1499 Adams St., Chicago, Ill.

CHANGES OF ADDRESS.

Aldrich, Thomas B., care Parke, Davis & Co., Detroit, Mich.
Atwood, W. P., 17 19th St., Lowell, Mass.
Baldwin, Herbert B., 9 and 11 Franklin St., Newark, N. J.
Bosart, L. W., Jr., care W. W. Simmons, 6018 Washington
Ave., Chicago, Ill.
Bucher, John E., Brown Univ., Providence, R. I.
Carr, Robert F., 31 Rialto Bldg., Chicago, Ill.
Corse, W. M., 73 Horton Ave., Detroit, Mich.
Craig, Archibald, 13 Congress St., Pittsburg, Pa.
Doyle, Miss Aida M., 3525 Eslin Ave., Mount Pleasant, Wash-
ington, D. C.
Fischer, Louis A., National Bureau of Standards, Washington,
D. C.
Flintermann, R. F., 2428 N. Hermitage Ave., Chicago, Ill.

Fosdick, E. H., 825 W. 17th St., Los Angeles, Cal.
Fuller, Fred D., 29 Lyceum St., Geneva, N. Y.
Garrigues, W. E., 214 W. 42nd St., New York City.
Grabfield, Joseph P., care Nelson Morris, and Co., U. S. Yards; Chicago, Ill.
Hess, Wm. H., Fenton, Genesee Co., Mich.
Hewson, James H., 142 Orchard St., Newark, N. J.
Hibbard, P. L., 163 Park Ave., Waukegan, Ill.
Kittredge, H. G., 42 Linden Ave., Dayton, O.
Lazell, E. W., 1110 Stephen Girard Bldg., Philadelphia, Pa.
Levine, Edmund J., care The Fiberloid Co., 636-8 Broadway, New York City.
MacPherran, R. S., Allis-Chalmers Co., Milwaukee, Wis.
Neilson, Thomas, Trinity Copper Co., Kennett, Shasta Co., Cal.
Norton, Mrs. Alice P., School of Education, Univ. of Ill., Chicago, Ill.
Palmer, Chase, Central Univ. of Ky., Danville, Ky.
Pough, F. H., 146 Hicks St., Brooklyn, N. Y.
Root, Wm. L., Newark High School, Newark, N. J.
Sarles, Edgar H., 21st St. and Stewart Ave., Chicago, Ill.
Schimpf, Henry W., 404 W. 34th St., New York City.
Schlichting, Emil, 646 Broadway, Milwaukee, Wis.
Shepherd, Frank I., University P. O., Los Angeles Cal.
Smither, F. W., 30 Cole Bldg., Nashville, Tenn.
Spencer, G. Carl, 98 Grove St., Lowell, Mass.
Tolman, L. M., 2818 13th St., N. W., Washington, D. C.
Tufts, J. L., Hudson River Works, Edgewater, N. J.
Von Egloffstein, C., 58 Garden St., Brooklyn, N. Y.
Waters, Campbell E., Johns Hopkins Univ., Baltimore, Md.
Woodworth, E. Harold, 135 So. Main St., Jamestown, N. Y.

ADDRESS WANTED.

Bernheim, Geo. B., formerly of 74 E. 79th St., N. Y. City.

Issued with October Number, 1901.

Proceedings.

MINUTES OF THE TWENTY-FOURTH GENERAL MEETING OF THE AMERICAN CHEMICAL SOCIETY.

The Twenty-Fourth General Meeting of the American Chemical Society was held in Room 14 of the High School Building, corner of Nineteenth and South Streets, Denver, Colorado, August 26 and 27, 1901.

The first session, a joint session with Section C of the American Association for the Advancement of Science, was called to order Monday, August 26th, at 11.30 A.M., by Vice-President John H. Long, of Section C, who introduced Mr. Franklin Guiterman, superintendent of The American Smelting and Refining Co. Mr. Guiterman extended to the visiting chemists a few cordial words of welcome, which were responded to by President F. W. Clarke in behalf of the American Chemical Society, and Vice-President Long in behalf of Section C.

The joint session was then adjourned and, after a few minutes spent in organizing Section C, the American Chemical Society was called to order by Professor Long at the request of President Clarke.

Chas. Baskerville, chairman, presented the final report of the Census Committee for the Twenty-fifth Anniversary.

President Clarke then returned and took the chair, and the report was discussed by Messrs. McPherson, Baskerville, and Hale. Upon motion of Mr. Hale the report was accepted by the Society and referred to the Committee on Papers and Publications.

After some announcements the morning session was adjourned.

The afternoon session was called to order by President Clarke at 2 o'clock. The following named papers were read by their authors: "A Summary of the Analysis of Some Massive and Eruptive Rocks of Boulder County, Colorado," by Chas. Skeele Palmer. "Optical Rotations of Certain Tartrates in Glycerol,"

by John H. Long. "Recent Developments in Physical Chemistry," by Wilder D. Bancroft.

TUESDAY, AUGUST 27TH.

The morning session was called to order by President Clarke at 10.05 o'clock. A paper on "The Atomic Volume Curve in Relation to the Periodic Sequence," by Chas. Skeele Palmer, was read by its author and discussed by Messrs. Clarke and Lachman.

This was followed by a "Report on Some of the Mineral Waters of the Philippine Islands," by G. B. Frankforter and some announcements by the secretary of Section C.

Mr. Kepner, of Denver, then called attention to an exhibit of apparatus by the Denver Fire Clay Co., which was on the third floor of the building, and invited the chemists to inspect it at their convenience.

A paper on "Proper Methods of Teaching Physical Chemistry," by Wilder D. Bancroft, was presented by the author and discussed by Messrs. Long, Bancroft, Lachman, Hale, Brown, Clarke, and Frankforter.

On motion of Professor Long, the president of the Society, Professor F. W. Clarke, and the secretary, Dr. Albert C. Hale, were elected to represent the Society in the Council of the American Association for the Advancement of Science, in accordance with an amendment to its constitution passed by the Association at its morning session, authorizing the increase of its Council by the addition of two representatives from each of the affiliated societies, subject to the condition that said representatives must be fellows of the Association.

After some announcements a paper "On the Existence of a New Element Associated with Thorium," by Chas. Baskerville, was read by its author and discussed by Messrs. Brown, Clarke, Baskerville, and Bancroft.

After some further announcements by the secretary the morning session was adjourned.

The afternoon session was called to order at 2.10 P.M. by President Clarke.

A paper on "Some Suggestions for Improvement in Instruction in Technical Chemistry," by Arthur Lachman, was read by the author.

A paper on "Some Observations on the Teaching of Chemistry," by Chas. Skeele Palmer, was then presented and the two

papers were discussed by Messrs. McPherson, Clarke, Brown, Lachman, and Hale.

A paper on "Chemistry in the High School," by Fredus N. Peters, was presented by the secretary in the absence of its author.

A paper on "Chemistry in Manual Training High Schools," by Armand R. Miller, was read by the author and discussed by Messrs. Fuller, Miller, Slosson, and Frankforter.

The abstract of a paper on the "Origin and Use of Natural Gas at Manitou, Colorado," by William Strieby, was read by the secretary in the absence of the author, as was also an abstract of a paper entitled "Notes on the Chlorides of Ruthenium," by Jas. Lewis Howe.

Arthur Lachman then presented a paper on "Some New Laboratory Furniture," which was discussed by Messrs. Frankforter and Hale.

After some announcements, upon motion of the secretary, the thanks of the Society were unanimously voted to the chairman and other members of the Local Committee of Arrangements for the Meeting; the Board of Education of the City of Denver, the superintendent of schools, and the principal of the East Denver High School; the officers and managers of the Argo, Grant, and Globe Reduction Works; Mr. Franklin Guiterman, superintendent of the American Smelting and Refining Co.; Mr. J. D. Hawkins, superintendent of the Colorado-Philadelphia Reduction Co.; and The Denver Fire Clay Co.

Professor Chas. S. Palmer, chairman of the Local Committee of Arrangements for entertaining the chemists, expressed his appreciation of the vote of thanks, and the Twenty-fourth General Meeting of the Society was then adjourned.

On Wednesday afternoon the chemists visited the smelting works (Globe, Grant, and Argo) in the vicinity of Denver. A special train was furnished by the courtesy of the Colorado and Southern Railroad Company, and was in charge of Mr. C. L. Wellington, traffic manager. Mr. Franklin Guiterman, of the American Smelting and Refining Company, with the aid of Professor Chas. S. Palmer, conducted the party.

A subscription dinner was held on Wednesday evening at 7 o'clock, at the University Club, corner of Seventeenth and Sherman Avenues. About forty chemists and their friends were present.

ALBERT C. HALE, *Secretary.*

COUNCIL.

The Council of the American Chemical Society was called to order by President Clarke at 4.50 P.M., August 26, 1901, in Room 14 of the High School Building, Denver, Colorado.

As there was no quorum, various matters were discussed informally, but no action was taken.

The Council adjourned at 6.15 P.M.

ALBERT C. HALE, *Secretary.*

NAMES PROPOSED FOR MEMBERSHIP.

- Alexander, George E., 1736 Champa St., Denver, Colo.
 Alleman, Gellert, Washington Univ., St. Louis, Mo.
 Amehl, Lawrence L., 5407 Black St., Pittsburg, Pa.
 Barkur, Henry M., Copper Cliff, Ont.
 Batchelder, Gilbert N., Box 554, Montreal, Canada.
 Berry, George M., 5523 Center Ave., Pittsburg, Pa.
 Black, Homer V., Ga. School of Tech., Atlanta, Ga.
 Blanchard, Wm. M., DePauw Univ., Greencastle, Ind.
 Bolser, Charles E., Dartmouth Coll., Hanover, N. H.
 Collins, Paul, Raleigh, N. C.
 Cromlish, Albert Leighton, 21 W. North St., New Castle, Pa.
 Furman, H. Van F., 218 Boston Bldg., Denver, Colo.
 Gleason, C. A., Shelby, O.
 Goldthwaite, Nellie E., South Hadley, Mass.
 Guiterman, Franklin, 835 Ogden St., Denver, Colo.
 Hensel, Samuel T., 801 E. Colfax Ave., Denver, Colo.
 Hodgkins, David Harwood, Phillipsdale, R. I.
 Hopkins, Frank W., Meeker, Colo.
 Johnson, Edward M., Grant Plant, Denver, Colo.
 Kelly, Wm. E., 2061 7th Ave., N. Y. City.
 Kepner, Harry V., 2103 Gilpin St., Denver, Colo.
 Lachman, Arthur, Eugene, Ore.
 Low, Wilson H., care of Cudahy Packing Co., South Omaha, Nebr.
 McCullough, Edwin C., 452 E. 3rd St., Dayton, O.
 Mory, A. V. H., care of Armour Packing Co., Kansas City, Kans.
 Mulliken, Harry S., Monterey, N. L., Mexico.
 Myers, Rollin Guizot, 88 W. Main St., Shelby, O.
 Nakayama, Takakichi, care of Japanese Consulate, 99 Nassau St., N. Y. City.
 Patterson, A. M., Rose Poly. Inst., Terre Haute, Ind.
 Patton, Arthur L., Boulder, Colo.
 Remington, Walter W., Montclair, Colo.
 Richardson, Charles Henry, Dartmouth Coll., Hanover, N. H.
 Scott, W. G., care of J. I. Case T. M. Co., Racine, Wis.

Seidell, Atherton, Dept. of Agr., Washington, D. C.
Skinner, Lewis B., Colorado Springs, Colo.
Separk, Edward A., Ironwood, Mich.
Spearlin, Oscar L., S. C. Cotton Oil Co., Columbia, S. C.
Squire, George B., El Paso, Texas.
Sullivan, Thomas V., 1530 9th St., N. W., Washington, D.C.
Vanier, George P., 229 S. 4th St., Steelton, Pa.
Warren, A. Sydney, 1 Austin St., Buffalo, N. Y.
Wiigsohn, Mr., Shelby, O.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Annear, John B., Boulder, Colo.
Argall, Philip H., Boulder, Colo.
Henry, Carl D., Boulder, Colo.
Thayer, Harry S., Greeley, Colo.

NEW MEMBERS ELECTED JUNE 25, 1901.

Dewey, Elbert E., 518 Washington Boulevard, Chicago, Ill.
Goodmar, Julian H., 121 E. 23rd St., N. Y. City.
Hyman, Leonard W., 342 S. Pearl St., Albany, N. Y.
Reckhart, D. W., Box 88, El Paso, Texas.
Stalnaker, Edwards S., Thomas, W. Va.
Strange, William W., Oberlin, O.
Terry, H. Warren, Jr., 2029 Mt. Vernon St., Phila.
Turner, Herbert S., Oglesby, La Salle Co., Ill.
Watson, Charles A., Raleigh, N. C.

ASSOCIATES ELECTED JUNE 25, 1901.

Flanders, F. F., Pullman, Wash.
Reid, Burton 1103 W. 40th St., Kansas City, Mo.
Young, E. H., Pullman, Wash.

NEW MEMBERS ELECTED SEPTEMBER 9, 1901.

Hosch, George E., 904 St. John's Pl., Brooklyn, N. Y.
Lyon, A. E., Care of Chiapos Mining Co., Teapa, Tabascos,
Mex.
Potter, Nathan S., Jr., Cement City, Mich.
Schlundt, Herman, Madison, Wis.
Stuart, Duncan, 1937 13th St., N. W., Washington, D. C.
Wells, J. Walter, Provincial Assay Office, Belleville, Ontario.

ASSOCIATE ELECTED SEPTEMBER 9, 1901.

Kimball, Sherman, Palo Alto, Cal.

CHANGES OF ADDRESS.

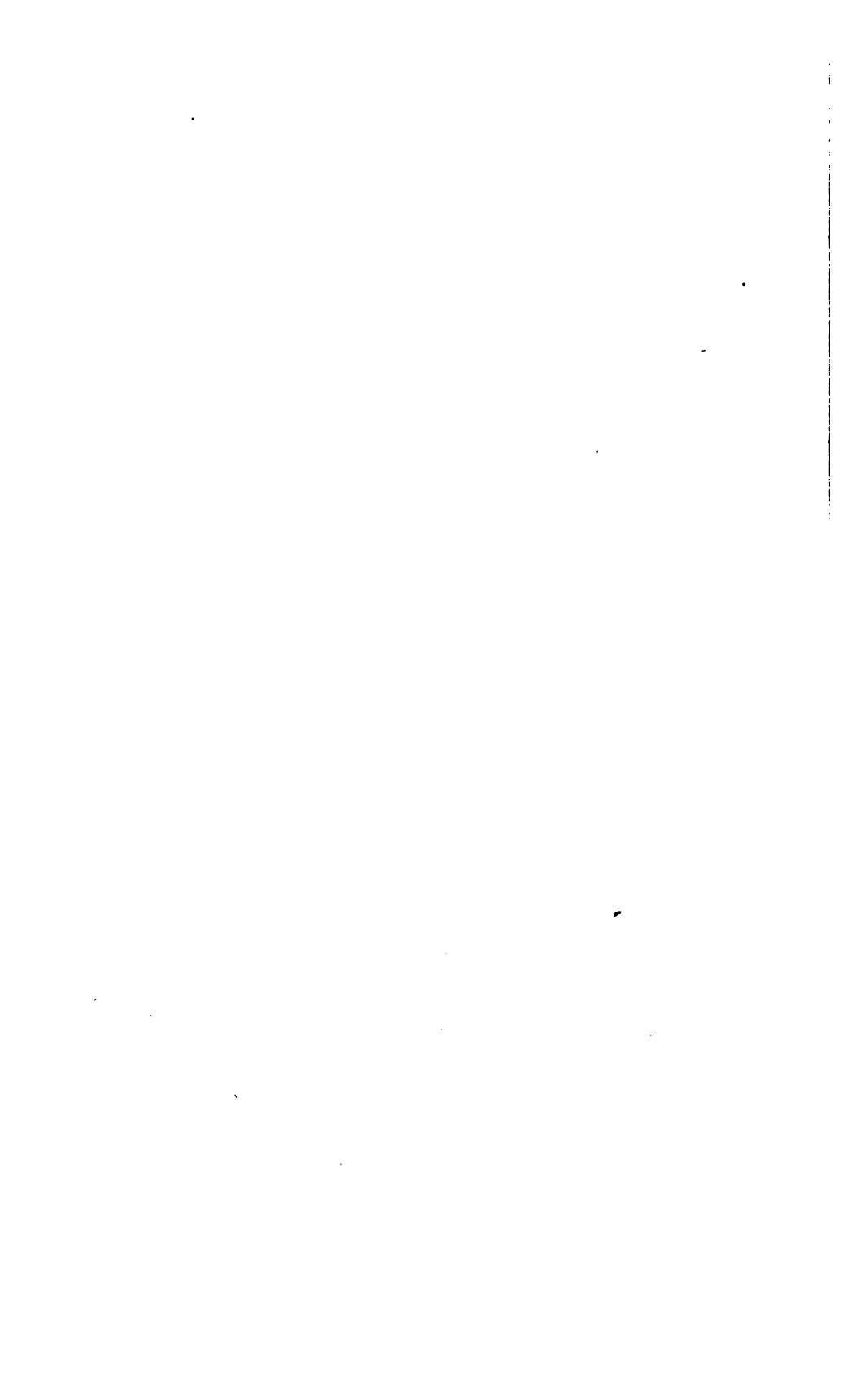
Adams, Maxwell, Chico, Cal.
Austin, N. M., Duquesne, Pa.

- Barrows, E. R., Brandt, Susquehanna Co., Pa.
 Benson, D. H., Box 145, So. Jacksonville, Fla.
 Bizzel, J. A., 305 Dryden Road, Ithaca, N. Y.
 Bowman, Walker, 39 Cortlandt St., N. Y. City.
 Briggs, T. Lynton, 316 Bowne Ave., Flushing, N. Y.
 Carnell, Wm. C., Tacony Chem. Wks., Bridesburg, Philadelphia, Pa.
 Cary, Edward A., care Puget Sound Reduction Co., Everett, Wash.
 Clark, Alfred N., Box 145, Alma, Mich.
 Cottle, George T., 186 Christian St., Wallingford, Conn.
 Darke, Jesse M., 551 Essex St., Lynn, Mass.
 Davis, R. O. E., Chapel Hill, N. C.
 Dorr, John V. N., 918 Equitable Bldg., Denver, Colo.
 Falk, Kaufman G., 63 E. 74th St., N. Y. City.
 Ferris, W. S., 227 Wisconsin St., Milwaukee, Wis.
 Gass, James K., 4321 Cloud St., Frankford, Pa.
 Getman, F. H., Johns Hopkins Univ., Baltimore, Md.
 Given, Arthur, 1937 13th St., N. W., Washington, D. C.
 Glasoe, P. M., Box 723, Northfield, Minn.
 Godley, Geo. McM., 90-101 West 80th St., N. Y. City.
 Goodell, Geo. A., 284 St. Nicholas Ave., N. Y. City.
 Gore, Herbert C., Freeport, Ill.
 Hale, Albert C., 352A Hancock St., Brooklyn, N. Y.
 Hopkins, Erastus, 60 William St., Worcester, Mass.
 Irwin, E. P., Boise, Idaho.
 Koch, F. C., 208 W. Elm St., Urbana, Ill.
 Kunze, W. F., Red Wing, Minn.
 Leffmann, Henry, 119 S. 4th St., Philadelphia, Pa.
 Mahon, R. W., N. Y. C. and H. R. R., West Albany, N. Y.
 Mathewson, E. P., care Amer. Sm. and Ref. Co., 71 Broadway, N. Y. City.
 Matthews, J. Merritt, 225 So. 45th St., Philadelphia, Pa.
 Miller, Armand R., 620 Woodland Ave., Kansas City, Mo.
 Mommers, Richard, Rockford, Ill.
 Moody, Herbert R., Hobart College, Geneva, N. Y.
 Motion, John, Valvoline Oil Co., Edgewater, N. J.
 Parmelee, H. C., 524 E. 30th Ave., Denver, Colo.
 Pemberton, Ralph, 1947 Locust St., Philadelphia, Pa.
 Rand, Charles L., 105 Quarry St., Ithaca, N. Y.
 Reese, Herbert J., Bozeman, Mont.
 Reubens, Chas. M., Sec'y Brady Brass Co., 202 Tenth St., Jersey City, N. J.
 Richardson, W. D., care of Swift & Co., National Stock Yards, East St. Louis, Ill.
 Riddell, D. F., Sioux Falls Coll., Sioux Falls, S. D.
 Ripley, Philip F., care of Assabet Mills, Maynard, Mass.
 Rising, H. R., Newark, N. J.

Ryan, I., 452 Fairmount Ave., Jersey City, N. J.
Schoonmaker, H., 917 Race St., Cincinnati, O.
Shepherd, E. S., 205 Hazen St., Ithaca, N. Y.
Sinkinson, J. Dawson, 645 Marcy Ave., Brooklyn, N. Y.
Smith, Edward S., 826 W. 43rd St., Chicago, Ill.
Sparks, John C., De La Vergne Refrigerating Machine Co.,
foot of E. 138th St., N. Y. City.
Stocker, John H., 189 Jefferson Ave., Brooklyn, N. Y.
Strahorn, A. T., Box 101, Norfolk, Nebr.
Thomas, W. H., Jr., Passaic Print Works, Passaic, N. J.
Tingle, J. Bishop, Ill. College, Jacksonville, Ill.
Torrey, Charles A., Jr., 17 Park Vale, Brookline, Mass.
Touzalin, Leslie A., Rose Poly. Inst., Terre Haute, Ind.
Wagner, Theodore B., 1444 Wilson Ave., Chicago, Ill.
White, Alfred H., 1003 University Ave., Ann Arbor, Mich.
Wigfall, E. Newton, 83 E. Lacrosse Ave., Lansdowne, Pa.
Willey, Ogden G., care Crane Co. Lab., 52 Judd St., Chicago,
Ill.

ADDRESSES WANTED.

Hanson, Charles A., formerly care of Fleischmann & Co.,
Riverside, Cincinnati, Ohio.
Remington, J. Percy, formerly of 65 Columbia Heights, Brook-
lyn, N. Y.
Waterman, C. N., formerly of 134 50th St., Chicago, Ill.



Issued with November Number, 1901.

Proceedings.

COUNCIL.

The winter meeting of the Society will be held in Philadelphia, on Monday and Tuesday, December 30 and 31, 1901.

NAMES PROPOSED FOR MEMBERSHIP.

- Arsem, William C., 13 N. College St., Schenectady, N. Y.
Beers, Frank Troxell, Emporium, Pa.
Bull, Irving C., Box 294, Middletown, N. Y.
Burgess, Charles F., Engineering Building, Madison, Wis.
Burroughs, Karl, Rumford Falls, Me.
Cassady, V. K., Armour Glue Works, Chicago, Ill.
Chambers, Victor J., Columbia Univ., N. Y. City.
Crayen, Gustav, 446 W. 23rd St., New York City.
Daniels, Frank C., 40 R St., N. E., Washington, D. C.
Davis, Emerson, 515 Cass Ave., Detroit, Mich.
Dean, John Godfrey, Cement City, Mich.
DuPont, Irene, 788 Broad St., Newark, N. J.
Durkee, Frank W., Tufts College, Mass.
Easterbrooke, Frank D., Raritan Copper Works, Perth Amboy, N. J.
Exner, Franz F., 118 N. 58th St., Philadelphia, Pa.
FitzGerald, Francis A. J., Niagara Falls, N. Y.
Forbes, Howard C., 4 State St., Boston, Mass.
Foster, Mary L., Maywood, N. J.
Goddard, John Newton, Apartado 101, Monterey, N. L., Mexico.
Goodrich, C. C., Akron, Ohio.
Gross, John, Sombrerete, Zac., Mexico.
Hampton, Frederick T., Hill City, Tenn.
Heacock, E. A., High School, Topeka, Kan.
Horton, William A., 96 Prospect Place, Brooklyn, N. Y.
Jackson, Henry A., 419 W. 118th St., N. Y. City.
Kolb, Theodore B., 616 North Main St., Elmira, N. Y.
Laist, Frederick, Santa Ana, Cal.
Loub, Charles M., 62 Maiden Lane, New York City.
Mitchell, John P., Box 282, Palo Alto, Cal.
Mojonnier, Timothy, 918 W. Green St., Urbana, Ill.
Nagelvoort, J. B., care Nickells-Stone Chem. Co., New Orleans, La.

Nelson, John M., Expt. Sta., Univ. of Nebr., Lincoln, Neb.
 Nickels, Arthur R., care U. S. R. R. Co., Colorado Springs,
 Colo.

Palmer, (Miss) Rose A., 1408 31st St., N. W., Washington,
 D. C.

Pope, Frank, care the Dunwoody Bros. Soap Co., Denver,
 Colo.

Prohaska, Otokar L., 361 S. Winchester Ave., Chicago, Ill.

Slade, Henry B., Univ. of Nebr., Expt. Sta., Lincoln, Nebr.

Snell, John F., Univ. of Cincinnati, Cincinnati, O.

Turner, B. Bernard, Univ. of Mo., Columbia, Mo.

Von Rücker, Hermann, 163 E. 56th St., New York City.

Wiley, Samuel W., 150 Main St., Amherst, Mass.

Wilkinson, L. W., Tulane Univ., New Orleans, La.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Bache, A. Wilbur, 1225 11th St., Washington, D. C.

Breneman, Harry C., 413 W. 117th St., N. Y. City.

Craser, Frederick V. D., 195 Clinton St., Brooklyn, N. Y.

Danziger, J. L., 2549 8th Ave., N. Y. City.

Dickie, Albert E., 566 Macon St., Brooklyn, N. Y.

Evans, L. P., Pinole, Contra Costa Co., Cal.

Lewis, Henry F., Hamil's Point, Lake Joseph, Winskoka,
 Ontario, Canada.

Mersereau, Gail, 242 W. 123rd St., N. Y. City.

Phipps, Charles B., East Rockaway, L. I., N. Y.

Tibbals, Austin, 353 W. 119th St., N. Y. City.

Whitfield, Fred. C., 124 Hicks St., Brooklyn, N. Y.

NEW MEMBERS ELECTED OCTOBER 28, 1901.

Alexander, George E., 1736 Champa St., Denver, Colo.

Alleman, Gellert, Washington Univ., St. Louis, Mo.

Arnold, Lawrence L., 5407 Black St., Pittsburg, Pa.

Barkur, Henry M., Copper Cliff, Ont.

Batchelder, Gilbert N., Box 554, Montreal, Canada.

Berry, George M., 5523 Center Ave., Pittsburg, Pa.

Black, Homer V., Georgia School of Tech., Atlanta, Ga.

Blanchard, Wm. M., DePauw Univ., Greencastle, Ind.

Bolser, Charles E., Dartmouth College, Hanover, N. H.

Collins, Paul, Raleigh, N. C.

Cromlish, Albert L., 21 W. North St., New Castle, Pa.

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Goldthwaite, Miss Nellie E., South Hadley, Mass.

Guiterman, Franklin, 835 Ogden St., Denver, Col.

Hensel, Samuel T., 801 E. Colfax Ave., Denver, Col.

Hodgkins, David H., Phillipsdale, R. I.

Hopkins, Frank H., Meeker, Col.

Johnson, Edward M., Grant Plant, Denver, Col.

Kelly, Wm. E., 2061 7th Ave., N. Y. City.
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Lachman, Arthur, Eugene, Oregon.
Low, Wilson H., care of Cudahy Packing Co., South Omaha, Neb.
McCullough, Edwin C., 452 E. 3rd St., Dayton, O.
Mory, A. V. H., care of Armour Packing Co., Kansas City, Kans.
Mulliken, Harry S., Monterey, N. L., Mexico.
Myers, Rollin G., 88 W. Main St., Shelby, O.
Nakayama, Takakichi, care of Japanese Consulate, 99 Nassau St., N. Y.
Patterson, A. M., Rose Poly. Inst., Terra Haute, Ind.
Patton, Arthur L., Boulder, Col.
Remington, Walter W., Montclair, Col.
Richardson, Charles H., Dartmouth College, Hanover, N. H.
Scott, W. G., care of J. I. Case T. M. Co., Racine, Wis.
Seidell, Atherton, Dept. of Agr., Washington, D. C.
Skinner, Lewis B., Colorado Springs, Col.
Separk, Edward A., Ironwood, Mich.
Spearlin, Oscar L., S. C. Cotton Oil Co., Columbia, S. C.
Squire, George B., El Paso, Texas.
Sullivan, Thomas V., 1530 9th St., N. W., Washington, D. C.
Vanier, George P., 229 S. 4th St., Steelton, Pa.
Warren, A. Sydney, 1 Austin St., Buffalo, N. Y.

ASSOCIATES ELECTED OCTOBER 28, 1901.

Annear, John B., Boulder, Col.
Argall, Philip H., Boulder, Col.
Henry, Carl D., Boulder, Col.
Thayer, Harry S., Boulder, Col.

CHANGES OF ADDRESS.

Amberg, A. J., Boston, Mass.
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Baekeland, Leo, "Snug Rock," N. Broadway (Harmony Park),
Yonkers, N. Y.
Balch, Dr. Alfred W., Surgeon U. S. Navy, care of Navy
Dept., Washington, D. C.
Beck, Oscar C., 330 18th Ave., Denver, Col.
Belden, A. W., Tenn. C. I. & R. R. Co., Robertstown Fur-
naces, Bessemer, Ala.
Cady, H. B., Box 586, Bay City, Mich.
Campbell, Archibald, 3312 Hackberry St., Walnut Hills, Cin-
cinnati, O.
Case, Elisha W., 266 North Central Park Ave., Chicago, Ill.
Clark, Edmund, 426 Sanford Ave., Flushing, N. Y.

- Clark, H. A., Haskell Institute, Lawrence, Kans.
 Cohoe, Wallace P., McMaster Hotel, Toronto, Canada.
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 Craig, A. G., Columbia University, N. Y. City.
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 Dorr, John V. N., 459 So. 15th St., Denver, Colo.
 Dunlap, Fred. L., 717 Arbor St., Ann Arbor, Mich.
 Dunn, Willis A., 1030 So. Hope St., Los Angeles, Cal.
 Ebaugh, W. Clarence, Kenyon College, Gambier, O.
 Ellery, James B., Duquesne, Pa.
 Evans, Ernest, care National Steel Co., Zanesville, Ohio.
 Hand, W. F., 355 W. 119th St., N. Y. City.
 Hanson, Charles A., Göteborgs Jäst-Aktiebolag, Göteborg, Sweden.
 Hardin, W. L., 750 W. Market St., Lima, Ohio.
 Hartwell, Burt L., 3713 Woodland Ave., Philadelphia, Pa.
 Haven, Frank S., 603 Farmington Ave., Hartford, Conn.
 Hicks, Edwin F., 233 W. 44th St., New York City.
 Hubbard, G. C., Columbia Univ., New York City.
 Kohr, Donald A., 452 E. 3rd St., Dayton, O.
 Leach, Mary F., 502 Forest Ave., Ann Arbor, Mich.
 Lengfeld, Felix, 202 Stockton St., San Francisco, Cal.
 Levene, P. A., Saranac Lake, N. Y.
 Miller, Armand R., 906 Park Ave., Kansas City, Mo.
 Moore, C. J., Western Maryland College, Westminster, Md.
 Morgan, Leonard P., A. and M. College, Stillwater, Okla.
 Parker, F. L., Jr., College of Charleston, Charleston, S. C.
 Peppel, S. V., Geol. Survey, Ohio State Univ., Columbus, Ohio.
 Poole, Hermann, 157 W. 105th St., New York City.
 Porter, Horace C., 41-A Irving St., Cambridge, Mass.
 Remington, J. Percy, 36 Doughty St., Brooklyn, N. Y.
 Riederer, H. S., 251 W. 95th St., N. Y. City.
 Rogers, Allen, 3605 Locust St., Philadelphia, Pa.
 Sloane, T. O'Conor, 49 Wall St., N. Y. City.
 Terry, H. Warren, Jr., 1707 St. Paul St., Baltimore, Md.
 Thayer, Harry S., Boulder, Colo.
 Thorburn, A. D., 55 Walnut St., Sta. D., Chicago, Ill.
 Van Brunt, Charles, 48 Brattle St., Cambridge, Mass.
 Watson, E. T., 964 Neil Ave., Columbus, Ohio.
 Weston, David B., 301 Seymour St., Lansing, Mich.
 Youtz, L. A., 523 W. 123d St., New York City.

DECEASED MEMBERS.

Dr. Philip S. Baker, of Greencastle, Ind., member of the Society since 1894, died September 2, 1901.

Mr. F. O. Matthiessen, of New York City, associate of the Society since 1876, died March 8, 1901.

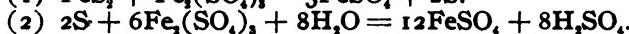
MEETINGS OF THE SECTIONS.

WASHINGTON SECTION.

The 128th regular meeting of the Washington Section of the American Chemical Society was held at the Cosmos Club Hall, Thursday evening, October 10th. The following program was presented :

"Pyrite and Marcasite," by H. N. Stokes.

Dr. Stokes stated that the physical characteristics by which these geologically important dimorphous forms of iron disulphide are distinguished are not always applicable, especially when they occur in the form of concretions. The paper describes a method by which they can always be determined, which consists in boiling an excess of the carefully prepared mineral with a standard solution of ferric ammonium alum, under absolute exclusion of air, until the alum is completely reduced. The reaction takes place in two stages :



The second reaction is always incomplete, only a portion of the sulphur being oxidized to sulphuric acid. Under the standard conditions the percentage of sulphur oxidized is 60.4 in the case of pyrite, and 18 in that of marcasite. The percentage of sulphur oxidized or the *oxidation coefficient* (ρ) is obtained from the equation

$$\rho = \frac{8.333 b}{c - a} - 25$$

which is deduced from the above equations, and in which a , b , and c represent the permanganate equivalents of the standard solution and of the ferrous iron and total iron of the resulting solution respectively. The proportion of the minerals in a mixture of both can be determined to within 1 to 3 per cent, by finding its oxidation coefficient and referring to an empirical curve of oxidation coefficients obtained by experiments with artificial mixtures. It was shown that the concretions described by geologists and mineralogists as marcasite are frequently pyrite, that the density affords no criterion of the composition, and that the hypothesis that most specimens of pyrite and marcasite, even when well crystallized, are mixtures of the two, paramorphs, is without foundation. It was also shown that their behavior towards cupric sulphate solutions is essentially similar and affords no evidence in support of the hypothesis of Brown that the chemical constitution of the two minerals, or the state of valency of the iron, is different. The full details are to be found in the recently published Bulletin No. 186 of the United States Geological Survey.

"Insolubility of Inorganic Salts in Hydrocarbons," by W. H. Seaman.

The author stated that several years ago he had the pleasure of announcing to the Society a generalization on the insolubility of glycerol ethers in glycerol. Now he is able to make a still more important generalization, that all inorganic salts are insoluble in hydrocarbons of the paraffine series. Fifty-three different salts have been kept in contact with benzine, kerosene, and soft paraffine for periods varying from two to six months without taking up a sufficient quantity of any salt to produce any residue, on evaporation in a watch-glass, that is visible by a pocket microscope.

The writer does not know of a single analysis of petroleum in which the presence of inorganic salts has been reported and in view of the fact that the petroleum has been in contact with some kinds of salts since it was formed, the natural conditions go far to support the generalization stated. Only in the case of ammonium carbonate was there any marked change; a brownish color was generally developed when in contact with this salt, the cause of which is not ascertained. At the suggestion of Prof. F. W. Clarke, anhydrous ferric chloride was prepared and tested, but the result was the same. The following is a list of the salts used:

Ammonium thiocyanate, bromide, phosphate, oxalate, carbonate, chloride, nitrate; antimony sulfide; barium chloride, nitrate, carbonate, dioxide; bismuth nitrate; arsenious acid; calcium chloride and nitrate; ferric chloride and ferrous sulfate; ferric ferrocyanide; magnesium carbonate; potassium bromide, cyanide, carbonate, iodide, bichromate, sulphate, chlorate; magnesium dioxide; potassium acetate; sodium bicarbonate, acetate, nitrate and sulphate; tartar emetic; zinc oxide; potassium ferrocyanide, chromate, hydroxide, picrate, chloride, nitrite; sodium borate, carbonate, chloride, hydroxide, nitrite, thiosulphate; ammonium molybdate, bichromate, sulphate; ammonia alum; magnesium sulphate and lithium carbonate.

I. S. MUNSON, *Secretary.*

Issued with December Number, 1901.

Proceedings.

COUNCIL.

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- Becket, Fred'k M., 318 W. 57th St., New York City.
Beistle, Charles P., 4752 Tacony St., Frankford, Philadelphia,
Pa.
Biddle, H. C., Univ. of Cal., Berkeley, Cal.
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Bixby, George L., Box 124, Collingswood, N. J.
Blakelock, David H., care Francis H. Richards, 9-15 Murray
St., N. Y. City.
Brawley, Margaret C., 6 Sachem St., Boston, Mass.
Cameron, Walter S., 239 W. 136th St., N. Y. City.
Carrier, Aubrey D., Covington, Va.
Clark, Harry A., Durham, N. H.
Dalton, N. Norman, Ivorydale, O.
Donald, William, Ridgefield Park, N. J.
Foulk, Chas. W., Ohio State Univ., Columbus, Ohio.
Fleming, Alexander, Scottdale, Pa.
Fuller, Henry C., The Madison, Madison Ave., Detroit, Mich.
Hartzell, L. J., Box 281, Philipsburg, Mont.
Herrmann, John Craven, 63 Orient Ave., Jersey City, N. J.
Higgins, Albert W., Saylesville, R. I.
Hollis, William H., 2528 Union St., San Francisco, Cal.
Hurst, Lewis A., 417 Third St., N. W., Washington, D. C.
Ingraham, William, 1003 Arrott St., Frankford, Philadelphia,
Pa.
Irving, Walter F., 266 W. 130th St., New York City.
Junga, Adelbert, 162 Garfield Pl., Brooklyn, N. Y.
Kirkland, Arch'd, 80 High St., Irvine, Ayrshire, Eng.
Landon, W. B., Susquehanna, Pa.
Leeming, Thomas L., Jr., 73 Warren St., New York City.
Lyman, James A., 525 Montgomery St., Portland, Ore.
McCullough, John E., National Steel Co., Youngstown, Ohio.
McFie, Robert A., The Nickel Company, Kirkintilloch, N. B.,
Scotland.
Myers, Ralph E., 3330 Walnut St., Philadelphia, Pa.

- Parks, Norman, Sarnia, Ontario, Canada.
 Penny, Charles L., Newark, Del.
 Prutzman, Paul W., 16th and Mississippi Sts., San Francisco,
 Cal.
 Rossati, Guido, 35 Broadway, New York City.
 Schlegel, John W., 602 E. 5th St., New York City.
 Shaw, Harlan P., Bridgewater, Mass.
 Smith, H. Carlton, 100 North Ave., Natick, Mass.
 Topping, Alanson N., 1017 Ann Ave., Kansas City, Kansas.
 Watters, Leon L., Univ. of Cincinnati, Cincinnati, Ohio.
 Widtsoe, John A., Logan, Utah.
 Withrow, James R., 4346 N. 7th St., Philadelphia, Pa.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

- Blair, Frank W., 95 Newbury St., Boston, Mass.
 Carleton, Spencer, 62 W. 49th St., New York City.
 Esquerré, Edmond, 116 W. 114th St., New York City.
 Hershey, Elam, Buffalo Union Furnace Co., Buffalo, N. Y.
 Lang, G. Bryant, 844 N. 20th St., Philadelphia, Pa.
 Mack, Joseph L., 1127 S. 48th St., Philadelphia, Pa.
 Miller, Howard E., Rose Poly. Inst., Terre Haute, Ind.
 Odell, J. R., 157 Huntington Ave., Boston, Mass.
 Richardson, Wm. D., Box 185, Fredericksburg, Va.
 Van Aldridge, Earl, 1122 Washtenaw Ave., Ann Arbor, Mich.
 Williams, R. S., 189 St. Botolph St., Boston, Mass.

NEW MEMBERS ELECTED NOVEMBER 29, 1901.

- Arsem, William C., 13 N. College St., Schenectady, N. Y.
 Beers, Frank T., Emporium, Pa.
 Bull, Irving C., Box 294, Middletown, N. Y.
 Burgess, Charles F., Engineering Building, Madison, Wis.
 Burroughs, Karl, Rumford Falls, Me.
 Cassady, V. K., Armour Glue Works, Chicago, Ill.
 Chambers, Victor J., Columbia University, N. Y. City.
 Crayen, Gustav, 446 W. 23rd St., N. Y. City.
 Daniels, Frank C., 40 R St., N. E., Washington, D. C.
 Davis, Emerson, 515 Cass Ave., Detroit, Mich.
 Dean, John G., Cement City, Mich.
 DuPont, Irenée, 788 Broad St., Newark, N. J.
 Easterbrooke, Frank D., Raritan Copper Works, Perth Amboy, N. Y.
 Exner, Franz F., 118 N. 58th St., Philadelphia.
 FitzGerald, Francis A. J., Niagara Falls, N. Y.
 Forbes, Howard C., 4 State St., Boston, Mass.
 Foster, Mary L., Maywood, N. J.
 Goddard, John N., Apartado 101, Monterey, N. L., Mexico.
 Goodrich, C. C., Akron, O.
 Gross, John, Sombrerete, Zacatecas, Mexico.

Heacock, E. A., High School, Topeka, Kansas.
 Horton, William A., 96 Prospect Pl., Brooklyn, N. Y.
 Jackson, Henry A., 419 W. 118th St., N. Y. City.
 Kolb, Theodore B., 616 N. Main St., Elmira, N. Y.
 Laist, Frederick, Santa Ana, Cal.
 Loub, Charles M., 62 Maiden Lane, N. Y. City.
 Mitchell, John P., Box 282, Palo Alto, Cal.
 Mojonnier, Timothy, 918 W. Green St., Urbana, Ill.
 Nagelvoort, J. B., care Nickells-Stone Chem. Co., New Orleans, La.
 Nelson, John M., Exp. Station, Univ. of Nebr., Lincoln, Nebr.
 Nickels, Arthur R., care U. S. R. R. Co., Colorado Springs, Colo.
 Palmer, (Miss) Rose A., 1408 31st St., N. W., Washington, D. C.
 Pope, Frank, care The Dunwoody Bros. Soap Co., Denver, Colo.
 Prohaska, Otokar L., 361 S. Winchester Ave., Chicago, Ill.
 Slade, Henry B., Exp. Station, Univ. of Nebr., Lincoln, Nebr.
 Snell, John F., Univ. of Cincinnati, Cincinnati, O.
 Turner, B. Bernard, Univ. of Mo., Columbia, Mo.
 Von Rücker, Hermann, 163 E 56th St., N. Y. City.
 Wiley, Samuel W., 150 Main St., Amherst, Mass.
 Wilkinson, L. W., Tulane Univ., New Orleans, La.

NEW MEMBERS ELECTED DECEMBER 5, 1901.

Durkee, Frank W., Tufts College, Mass.
 Gleason, C., Marvin Ave., Shelby, Ohio.
 Wihigsohn, Mr., Marvin Ave., Shelby, Ohio.

ASSOCIATES ELECTED NOVEMBER 29, 1901.

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 Breneman, Harry C., 413 W. 117th St.; N. Y. City.
 Cruser, Frederick V. D., 195 Clinton St., Brooklyn, N. Y.
 Danziger, J. L., 2549 8th Ave., N. Y. City.
 Dickie, Albert E. 566 Macon St., Brooklyn, N. Y.
 Evans, L. P., Pinole, Contra Costa Co., Cal.
 Lewis, Henry F., Hamil's Point, Lake Joseph, Winskoka, Ont., Can.
 Mersereau, Gail, 242 W. 123rd St., N. Y.
 Phipps, Charles B., East Rockaway, L. I., N. Y.
 Tibbals, Austin, 353 W. 119th St., N. Y. City.
 Whitfield, Fred. C., 124 Hicks St., Brooklyn, N. Y.

CHANGES OF ADDRESS.

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- Balch, Alfred W., care W. S. Reed, Leominster, Mass.
- Beck, Oscar C., Care of Colo. Iron Works, Denver; Colo.
- Bosart, L. W., Jr., Bond Hill, Ohio.
- Briggs, T. Lynton, 188 Central Ave., (Ingleside), Flushing, L. I., N. Y.
- Brown, J. W., Jr., Plöck Str. 77¹, Heidelberg, Germany.
- Cappou, Thomas Wm., 20 Broad Ave., Ossining, N. Y.
- Cohoe, Wallace P., McMaster Univ., Toronto, Can.
- Cook, Charles G., 394 Quincy St., Brooklyn, N. Y.
- Downey, James E., Hotel Newton, Worcester, Mass.
- Dreyfus, Wm., 162 E. 95th St., New York City.
- Dunn, W. A., 1023 S. Bonnie Brae St., Los Angeles, Cal.
- Dustin, Guy K., 3604 Lake Ave., Chicago, Ill.
- Eccles, David C., Box 388, Pullman, Wash.
- Eldred, Frank R., 114 E. North St., Indianapolis, Ind.
- Fireman, Peter, Mo. School of Mines, Rolla, Mo.
- Freer, P. C., care of Hon. D. C. Worcester, Manila, P. I.
- Gass, James K., 2124 W. 2nd St., Chester, Pa.
- Grainger, William E., Box 51, Johnson City, Tenn.
- Haigh, Frederic, 141 Autumn St., Passaic, N. J.
- Hamilton, L. P., 1375 W. 24th St., Los Angeles, Cal.
- Havens, Franke S., care O. G. Johnson, 1143 Garden St., Hoboken, N. J.
- Hayes-Campbell, J., 23 Branch St., St. Louis, Mo.
- Hoffmann, P. C., Box 841, Charleston, S. C.
- Jordan, James O., 30 Huntingdon Ave., Boston, Mass.
- Lustig, A. L., Phillipsdale, R. I.
- Mather, S. T., 2 LaSalle Ave., Chicago, Ill.
- Myers, Wm. S., 12 John St., New York City.
- McKenzie, R. Monroe, 1219 Washington St., Hoboken, N. J.
- Nakayama, Takakichi, care Burgess Sulphite Fiber Co., Berlin, N. H.
- Parmelee, Cullen W., Seminary Place, New Brunswick, N. J.
- Parmelee, H. C., 524 E. 30th Ave., Denver, Colo.
- Pemberton, Ralph, 1947 Locust St., Philadelphia, Pa.
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- Pray, D. M., 24 Linden St., Allston, Mass.
- Redding, A. C., Tybo, Nye Co., Nevada.
- Redpath, Léon W., Parlin, N. J.
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- Roberts, Alfred E., 162 W. 116th St., New York City.
- Roller, H. C., care Ampère Electrochemical Co., Niagara Falls, N. Y.
- Rosentwist, B. G. A., Atherton St., Hyde Park, Mass.
- Ryland, Garnett, Converse College, Spartanburg, S. C.
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- Simmons, Ward W., 120 Pierrepont St., Brooklyn, N. Y.

Smith, Walter E., 158 Doyle Ave., Providence, R. I.
 Sticht, G. A. H., 723 Lafayette Ave., Brooklyn, N. Y.
 Torrey, C. A., 17 Park Vale, Brookline, Mass.
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 Trubek, M., 52 Beaver St., New York City.
 Tufts, J. L., Hudson Heights, N. J.
 Wagner, Theo., 1444 Wilson St., Ravenwood Sta., Chicago,

Ill.

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 Whittier, Charles T., 72 Brinckerhoff St., Jersey City, N. J.
 Worstall, R. A., care Chicago Varnish Co., Chicago, Ill.

ADDRESSES WANTED.

Williams, S. Everard, formerly of 4 Brimmer St., Boston, Mass.

DECEASED MEMBERS.

Mr. Stratford Burtt, of Brooklyn, N. Y., member of the Society since January, 1901, died March 15, 1901.

MEETINGS OF THE SECTIONS.

CINCINNATI SECTION.

The eighty-fifth meeting of the Cincinnati Section was held in Hanna Hall, Cincinnati University, on Tuesday, October 15, 1901, Vice-president Hochstetter presiding. Frank I. Shepherd, secretary of the section, resigned on account of his removal to California, and L. L. Watters was elected to fill the vacancy.

The papers read were :

1. "On Magnesium Amalgam as a Reducing Agent," by Professor Thomas Evans, who described its production and its action on nitrobenzene and other aromatic nitro bodies.
2. "Some Remarks on Thatcher's Method for Calculating the Weight of Precipitates without the Use of the Balance," by Dr. Alfred Springer. He gave the results of a number of determinations made by Thatcher's method, from which he concluded that it was well adapted for rapid technical analyses.

The paper was discussed by Messrs. Evans, Springer, and Watters.

The eighty-sixth meeting of the Cincinnati Section was held in Hanna Hall, Cincinnati University, on Friday evening, November 15, 1901, President Crane presiding.

The following papers were read:

1. "An Analysis of Garden Sage (*Salvia officinalis*)," by Dr. L. L. Watters. His analysis showed sage to contain 0.96 per cent. of volatile oil, 14.19 per cent. of proteid matter of which almost one-half was insoluble in water and in dilute caustic solution. Curiously, no starch was found, and in opposition to analyses previously made by Ilisch and Riga, no malic acid could be detected, while, contrary to other analysis, 4 per cent. of an "iron-greening" tannin was found.
2. "Some Observations on the Manufacture of Heavy Chemicals in Europe," by F. W. Weissmann. Mr. Weissmann described the technique of the manufacture of acids and alkali cement, etc., in the larger plants in Germany.

L. L. WATTERS, Secretary.

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